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Encapsulation and Controlled Release in Food Preservation

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I. INTRODUCTION

Additives are incorporated into foods for a variety of reasons. For ex... added to various foodstuffs in an effort to ward off the early onset of ... are used to prolong the shelf life of lipid-containing foods by protec... pholipids against oxidative degradation, flavoring and coloring agent... enhancing the sensory characteristics of the food, while various ca... employed to improve the rheological and textural properties of the p...

In recent years, there has been a growing trend toward reducing ... additives and, where possible, replacing those chemically derived w... of natural origin [1,2]. The use of synthetic antioxidants in foods, suc... (BHA) and butylated hydroxytoluene (BHT), is being reevaluated bec... their possible carcinogenic effects [3]. Thus, strategies have been de... fication, and identification of antioxidants from natural sources for use ... many natural ingredients are less potent at equivalent addition levels ... applicability than their synthetic counterparts. Thus, a novel strategy to ... range of application of many types of natural functional ingredients is ... delivery systems. Because of the wide availability of encapsulated in... whose development was thought to be technically unfeasible are now ... products of a process in which the active ingredient has been envelo... thereby conferring many useful properties to or eliminating undesirab... ingredient.

A. Basis of Encapsulation

Encapsulation has been used by the food industry for more than 60 ye... sulation technology in food processing includes the coating of minute ... acidulants, fats, and flavors) as well as whole ingredients (e.g., raisins, ... ucts), which may be accomplished by microencapsulation and macro-coa... The science of encapsulation deals with the manufacture, analytical e...

encapsulated products. Despite its long history, the technology that has been developed for the food industry remains relatively unsophisticated compared to many other fields of application. This is a consequence of the limitations imposed on the food industry for the use of edible, low-cost ingredients and processing.

King [4] notes that it is important for the food scientist to distinguish between encapsulation versus entrapment of food ingredients. He states that encapsulation may be defined as a process of forming a continuous thin coating around encapsulants (i.e., solid particles, droplets of liquids, or gas cells), which are wholly contained within the capsule wall as a core of encapsulated material. On the other hand, entrapment refers to the trapping of encapsulants within or throughout a matrix (e.g., gel, crystal), but a small percentage of the entrapped ingredients will normally be exposed at the particle surface, whereas this would not be so for the encapsulated product. The material that is entrapped is generally a liquid but could be a solid particle or gas and is referred to by various names, such as core material, payload, actives, fill, or internal phase (5). The material that forms the coating is referred to as the wall material, shell, or coating.

The food industry applies encapsulation for a number of reasons [6–8]:

1. Encapsulation/entrapment can protect the core material from degradation by reducing its reactivity to its outside environment (e.g., heat, moisture, air, and light).
2. Evaporation or transfer rate of the core material to the outside environment is decreased/retarded.
3. The physical characteristics of the original material can be modified and made easier to handle. For example, a liquid component can be converted to solid particles; lumping can be prevented, the core material can be distributed more uniformly throughout a mix by giving it a size and outside surface, hygroscopicity can be reduced; flowability and compression properties can be improved, dustiness can be reduced; and density can be modified.
4. The product can be tailor designed to either release slowly over time or release at a certain point (i.e., to control the release of the core material so as to achieve the property delay until the right stimulus).
5. The flavor of the core material can be masked.
6. The core material can be diluted when only very small amounts are required, yet still achieve a uniform dispersion in the host material.
7. It can be employed to separate components within a mixture that would otherwise react with one another.

B. Benefits and Types of Microcapsules

Microencapsulation is defined as the technology of packaging solids, liquids, or gaseous materials in miniature, sealed capsules that can release their contents at controlled rates under specific conditions [9,10]. The miniature packages, called microcapsules, may range from submicrometer to several millimeters in size and have a multitude of different shapes, depending on the materials and methods used to prepare them. Generally speaking, the microcapsule has the capability of modifying and improving the apparent shape and properties of a substance. More specifically, the microcapsule has the ability to preserve a substance in the finely divided state and to release it as occasion demands.

Microcapsules offer the food processor a means with which to protect sensitive food components, ensure against nutritional loss, utilize otherwise sensitive ingredients, incorporate unusual or time release mechanisms into the formulation, mask or preserve flavors and aromas, and transform liquids into easily handleable solid ingredients [11]. The unusual properties afforded by encapsulated ingredients provide the food technologist with greater flexibility and control in developing foods that are more flavorful and nutritious to meet the expectations of today's consumers.

Various properties of microcapsules that may be changed to suit specific ingredient applications include composition, mechanism of release, particle size, final physical form, and cost. Before

considering the properties desired in encapsulated products, th[...] clear. In designing the encapsulation process, the following qu[...] eration.

1. What functionality should the encapsulated ingredi[...]
2. What kind of coating material should be selected?
3. What processing conditions must the encapsulated [...] ing its content?
4. What is the optimum concentration of the active [...]
5. By what mechanism will the ingredient be releas[...]
6. What are the particle size, density, and stability [...] ingredient?
7. What are the cost constraints of the encapsulated [...]

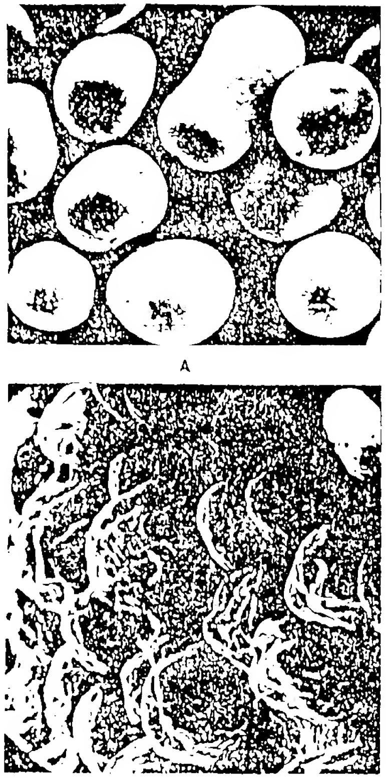
The architecture of microcapsules is generally divided in[...] classifications (Fig. 1). One such classification is known as matrix [...] structure in which a sphere is surrounded by a wall or membran[...] that of a hen's egg. In this design, the core material is buried to [...] microcapsule has been termed a single particle structure (Fig [...] microcapsules that have several distinct cores within the same ca[...] ous core particles embedded in a continuous matrix of wall mate[...] the aggregate structure (Fig. 1B). The particles in the aggregate s[...] material, and if one wishes, control of the particle size can be a[...] accomplished with numerous materials to improve size distribut[...] known design for a microcapsule is a multiwalled structure in w[...] layers can have the same, or quite different compositions. In this [...] around a core in order to achieve multiple purposes related to the [...] subsequent storage, and controlled release.

The theory and application of microcapsular delivery syste[...] neering techniques and scientific disciplines, thus making it diffi[...] the total effort being made in this field or to acquire a total picture [...] art of microencapsulation as it relates to the food industry and p[...] process of encapsulation. To accomplish this, a comprehensive ex[...] lating matrices currently used by the food industry is included. [...] tion, the advantages and disadvantages they offer as encapsulating a[...] are discussed. An in-depth examination of the various microencap[...] includes the processes of spray-drying, spray-cooling and spray [...] trusion, centrifugal extrusion, lyophilization, coacervation, co[...] cocrystallization, liposome entrapment, interfacial polymerization [...] terwards, encapsulated ingredients and their application to variou[...] reference to some of their common uses. Finally, what is meant [...] the mechanisms surrounding it is discussed.

II. THE ENCAPSULATION MATRIX

In order to encapsulate a food ingredient, the first requirement is th[...] ing material, referred to as the encapsulating matrix. In the literatur[...] to the coating material as the shell, wall material, or encapsulatin[...]

Coating substances, which are basically film-forming mater[...] variety of natural or synthetic polymers, depending on the materia[...] ties desired in the final microcapsules. The composition of the coa[...] nant of the functional properties of the microcapsule and of how [...]



A

B

Figure 1 Photomicrographs of different food ingredients: (A) microencapsulated potassium chloride; (B) vitamin A capsules in ethyl cellulose. (From Ref. 12.)

formance of a particular ingredient. An ideal coating material should exhibit the following characteristics:

1. Good rheological properties at high concentration and easy workability during encapsulation
2. The ability to disperse or emulsify the active material and stabilize the emulsion produced
3. Nonreactivity with the material to be encapsulated both during processing and on prolonged storage
4. The ability to seal and hold the active material within its structure during processing or storage
5. The ability to completely release the solvent or other materials used during the process of encapsulation under drying or other desolventization conditions

Table 1 Coating Materials for Encapsulation of Food Ingr

Carbohydrate	Starch, maltodextrins, corn syrup soli sucrose, cyclodextrins
Cellulose	Carboxymethylcellulose, methylcellul nitrocellulose, acetylcellulose, cellul cellulose acetate butylate phthalate
Gum	Gum acacia, agar, sodium alginate, ca
Lipid	Wax, paraffin, beeswax, tristearic acid monoacylglycerols, oils, fats, hardene
Protein	Gluten, casein, gelatin, albumin, hemo

Source: Ref. 12.

6. The ability to provide maximum protection to the mental conditions (e.g., oxygen, heat, light, humi
7. Solubility in solvents acceptable in the food indu
8. Chemically nonreactivity with the active material
9. Possession of specified or desired solubility prope properties of the active material from the capsule
10. Inexpensive, food-grade status

Because no single coating material can meet all of the crit coating materials are employed in combinations or modifiers such a chelating agents, and surfactants are added. Some commonly used c 1 are discussed in detail below.

A. Carbohydrates

The ability of carbohydrates to absorb and adsorb volatiles from t tenaciously during the drying process has important implications sulation. In fact, carbohydrates are the most commonly used coatin processes.

The mechanisms by which carbohydrates retain volatiles dur spray-drying as well as extrusion are not fully understood but mo actions [14]. It has been postulated that the formation of microreg contain highly concentrated solutions of carbohydrate and volatile of the carbohydrate through hydrogen bonding. This in turn creat volatiles [15]. For example, it has been reported that loss of volatile increased when the material changed from an amorphous solid to of cracks in the microregion structure might have accounted for t

The two major processes used for encapsulating food flavo sion [17]. Both of these depend primarily upon carbohydrates as t though one can find examples of encapsulation using fats (e.g., spra inorganics (fused silica) as wall materials, carbohydrates constitu matrices. While many compounds are classified as carbohydrate, d such compounds. Some are discussed under different headings an

1. Maltodextrins and Corn Syrup Solids

Starch is one of the most naturally abundant polymers found on e numerous food sources including corn, tapioca, potato, wheat, rice

Starch comprises polymers of glucose units linked together secondarily by α-(1→6) bonds. The two polymer types found in sta

polymer, and amylopectin, a branched-chain polymer. With its long, straight chains, amylose is known for forming strong, flexible films. On the other hand, due to its extensive branching, amylopectin is not a strong film former, but is noted for clarity and stability when forming gels and may show a slightly greater tendency towards absorption or binding of flavors. The content of amylose and amylopectin in starch granules varies depending on the source. When mixed with water and provided with enough heat, starch granules swell sufficiently to form pastes that can produce strong films, however, the viscosity of native starch is too high for most encapsulation processes.

Maltodextrins, $(C_6H_{12}O_5)_nH_2O$, are nonsweet nutritive polysaccharides consisting of α-(1→4) linked D-glucose units. However, in order to be termed maltodextrin, they must possess a reducing sugar content or "dextrose equivalence" (DE) of less than 20. Maltodextrins are prepared as white powders or concentrated solutions by partial hydrolysis of corn starch with safe and suitable acids or enzymes. If the DE equals or exceeds 20, they are referred to as corn syrup solids. DE, expressed as a percentage, is a measure of the reducing power of a sample compared to an equal weight of dextrose. Common designations of maltodextrins are 5, 10, 15, and 18 DE, while commercial corn syrup solids have 20, 25, 36, and 42 DE [19]. Products with a DE greater than 42 cannot be easily dried and hence are sold only as concentrates syrups. Because maltodextrins and corn syrup solids are so closely related to one another in terms of their physical and chemical properties as well as their applicability to food ingredient encapsulation, they will be discussed jointly. A flow diagram for the production of maltodextrins and corn syrup solids from corn starch is presented in Figure 2.

In the production of maltodextrins and corn syrup solids, starch is only partially hydrolyzed by acid or enzymes, thus, the resulting products are heterogeneous mixtures of various chain length glucose polymers. The higher the DE, the higher the concentration of product that can be put into

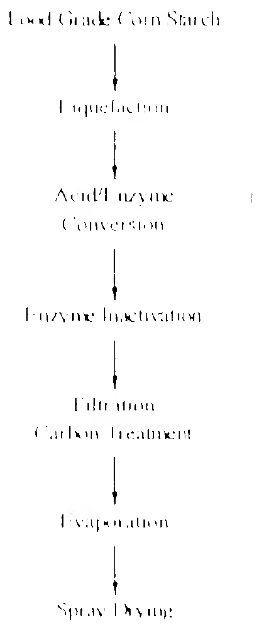


FIGURE 2 Flow diagram for the production of maltodextrin and corn syrup solids from corn starch. (From Ref. 19.)

solution. In spray-dried encapsulations, increased levels of solub
jor factor in the efficiency of production. In spray-dried encaps
and Reineccius [20] reported that the higher the DE of the corn sy
bility of the encapsulated oil. Bangs and Reineccius [21] found it
to be more efficient for spray-dried encapsulation of volatile artif
tulated that a balanced polymer length might aid in trapping the
let dries.

These hydrolyzed starches offer the advantages of being rel
one third that of modified starches), bland in flavor, and low in
However, the major problem with these products is the lack of en
most active materials (especially flavors) are insoluble in aqueous
emulsions. Thus, emulsion stability is viewed as an important co
ing material. Maltodextrins and corn syrup solids lack lipophilic c
emulsion stabilizing effect on water insoluble components [18].
and corn syrup solids do not retain volatile compounds well dur
typically perform more poorly, and retention often ranges betwe
capacity changes significantly as DE values change. Raja et
maltodextrins with varying DE values for encapsulating cardamon
tion of volatiles by maltodextrins and corn syrup solids was belie
capabilities (which is why they are sometimes referred to as carrie
encapsulation matrix must form a film around the droplets of acti
retain them during the drying process and water removal. It is cons
corn syrup solids have no emulsification properties, they produce e
in poor flavor retention during drying [24].

Maltodextrins and corn syrup solids vary greatly in protect
oxidation. There is a strong dependence of associative stability o
The encapsulated product with the highest DE is extremely stable a
without use of an antioxidant [20]. Several factors have been attri
afforded by high-DE coating materials. It has been considered th
permeable to oxygen and therefore offer better protection to encaps
also keep in mind that the presence of glucose in the encapsulatio
on the antioxidative properties.

2. Modified Starch

Starch presents an interesting situation with regard to flavor bind
forms helical structures, starch can entrap flavor molecules, thereby
[25]. However, starch is hydrophilic and hydrolysates derived fr
cation properties to the compound being encapsulated.

In its natural state, starch is cold water insoluble. One metho
cold water solubility is pyroconversion or dextrinization. In dext
granular form, generally in the presence of acid or alkali. Partial hy
as well as repolymerization to form more highly branched polyme
be varied to yield products with different solubility and viscosity
creased cold water solubility and lower solution viscosity than ge
if heated too long, the products become darker and stronger reaction
these strong color and flavor characteristics and a lack of lipophilic
trins less than ideal for encapsulation, especially of oil-based prod

The lack of emulsification properties of native starch creates t
is poor flavor retention. The fineness of the infeed emulsion has a
the extent of flavor retention during drying. The second problem re
emulsion once reconstituted in the final product. If the carrier prov
vor, then the flavor rapidly separates from the product and forms a
pound to function as an emulsifier, it must contain both lipophilic a

come this problem, starches can be modified chemically to change their functional characteristics. For example, the U.S. Food and Drug Administration (FDA) has approved the reaction of starch with 1-octenylsuccinic anhydride to form a modified starch containing both hydrophobic and hydrophilic groups. This level of substitution, usually in the range of 0.02%, results in a product that is vastly different from that of the native starch. The addition of lipophilic moieties along the starch polymer permits the formation of emulsions with tight alignment of the polymer around an oil droplet. This stabilization is extremely important for encapsulation of lipid products. Modified starch provides excellent retention of volatiles during spray drying and can be used at a higher infeed solids level than gum acacia (also known as gum arabic). While gum acacia is generally limited to use at about 35% infeed solids level, modified starch can typically be used at levels approaching 50% [18]. The high solids levels helps to reduce the loss of encapsulated ingredients and increases spray-dryer throughout.

The emulsification properties of lipophilic starches as well as the oil retention in the spray-dried powders are reported to be equal to or greater than that of gum acacia [26,27]. Modified starch also excels in promoting emulsion stability. One means of doing so is to produce small particle size droplets. Solutions of gum acacia produced an average emulsion droplet size of about 3 μm, and modified starch gave droplets of less than 2 μm. The emulsions made with modified starch were physically more stable than those made with the standard gum acacia [17]. Reineccius [18] pointed out that modified starches do have some disadvantages. For example, they are not considered natural for labeling purposes, they often have an undesirable off-flavor, and they do not afford good protection to oxidizable flavorings.

3. Cyclodextrins

Cyclodextrins are chemically and physically stable molecules formed by the enzymatic modification of starch. They have an ability to form complexes with a wide variety of organic compounds within their ringed structure. The ability of these unusual molecules to form inclusion complexes, which can change the physical and chemical properties of guest molecules, offers a variety of potential uses to the food industry. Although cyclodextrins have been studied for a century and their ability to form inclusion complexes has been recognized for at least 40 years, they were not utilized for food applications until the 1970s when Japan and Hungary began producing them commercially.

Cyclodextrins were discovered in 1891 when Villiers reported their appearance in rotting potatoes. In 1904, Schardinger characterized them as cyclic oligosaccharides and identified *Bacillus macerans* as the bacterium that produced cyclodextrin glycosyltransferase (CGTase), the enzyme responsible for the generation of cyclodextrins from starch. Because of Schardinger's studies, cyclodextrins were initially referred to as Schardinger dextrins. Of more significance was the fact that his work set the direction for future research, pointing it toward a study of the structure of cyclodextrins and their commercial production. French [28] has provided a detailed history of the development of cyclodextrins up to 1956.

Today, cyclodextrins are produced from starch by selected microorganisms such as *B. macerans* and *Bacillus circulans*, which have CGTase activity. After cleavage of starch by the enzyme, the ends are joined to form circular entities with β-(1→4) linkages. Because cyclodextrins are closed circular molecules, glucoamylases and β-amylases cannot hydrolyze them as there is no reducing end group, which is necessary to initiate hydrolysis. The cyclic dextrins formed contain six-, seven-, or eight glucose monomers; these are referred to as α-, β-, and γ-cyclodextrin, respectively. The glucose monomers are joined to one another in a doughnut-shaped ring, giving the cyclodextrins a molecular structure that is relatively rigid and has a hollow cavity of specific diameter and volume. Depending upon the enzyme used and the conditions under which the reaction is performed, the ratio of cyclodextrins can vary from various mixtures to a single cyclodextrin being formed.

Figure 3 shows the chemical structure of β-cyclodextrin, the predominant cyclodextrin produced by CGTase enzymes. Polar hydroxyl group of the glucose monomers are located on the rim of the molecule and are directed away from the cavity. These groups interact with water, giving cyclodextrins their aqueous solubility properties, and will interact with polar groups of some molecules to form hydrogen bonds. While the outer surfaces (top and bottom) are hydrophilic, the internal

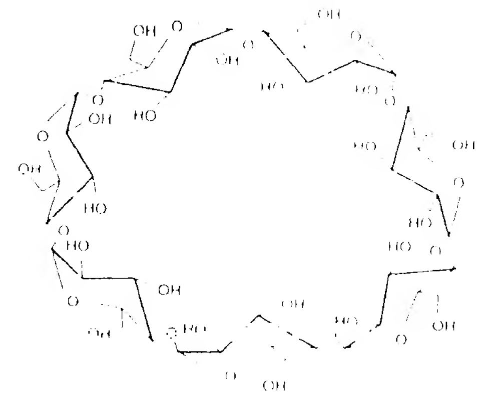


Figure 3 Chemical structure of β-cyclodextrin.

cavity has a relatively high electron density and is hydrophobic ...
glycosidic oxygen atoms being oriented to the interior of the cavi...

Organic molecules of suitable size, shape, and hydrophobicity ...
with cyclodextrins to form stable complexes. Several forces, such ...
phobic interaction, and dipole-dipole interaction, are involved in th...
the cyclodextrin cavity. These forces are sufficiently efficacious to ...
so secure that the guest molecule can be released from the comple...
tended effect [29].

The dimensions of the cyclodextrin's cavity allow some sele...
molecules. Strong binding results if more interaction occurs between ...
the guest molecule. If the molecule to be encapsulated is small con...
its surface is in contact with the walls and the full potential of the gu...
cyclodextrin is not realized. For molecules containing five or fewe...
ity of α-cyclodextrin affords more interaction between the molec...
complexation results than if β- or γ-cyclodextrin were used. On the o...
such as anthracene, fit into the cavity of the γ-cyclodextrin better th...
In fact sometimes molecules are too large to fit into the cavity of one ...
molecule might be totally excluded from the cavity or only a portion ...
molecule that can fit into the cavity, the stronger the binding. Sor...
cyclodextrins are summarized in Table 2 [30].

β-Cyclodextrin deserves special attention, as it is the most re...
preliminary studies it is generally used and is known to be able to ...
flavor ingredients of molecular masses ranging between 80 and 25...
that the molecules of nearly all natural spices and flavors fit into th...
cused on the ability of cyclodextrins to prevent the volatilization of f...
flavor extracts, and lipids. Nagatomo [32] reported that cyclodextrin...
for use in sausages and other meat products. Spices that have been ...
demonstrated controlled flavor release. In addition, thermal stability ...
to them. Nagatomo [32] also noted that cyclodextrins preserved the fla...
biscuits, citrus fruits, Japanese onions, garlic, celery, and a variety o...
reported that the strong odor of onion oil, garlic oil, and pyrazines wa...
but complexing with cyclodextrins prevented their flavor from bein...
leased their flavor directly into the mouth.

TABLE 2 Physical Properties of Cyclodextrins

Type of cyclodextrin	Physical properties						
	Number of glucose units	molecular weight	Molecular dimensions (Å)			Solubility at 25°C (g/100 ml H_2O)	$[\alpha]_D^{20}$ (H_2O, 1%)
			Inside diameter	Outside diameter	Height		
α	6	973	5.7	13.7	7.0	14.50	150.5°
β	7	1135	7.8	15.3	7.0	1.85	162.5°
γ	8	1297	9.5	16.9	7.0	23.20	117.4°

Source: Ref. 12.

Natural pigments such as carotenoids and anthocyanins [illegible] complex [12]. Pigments can be masked or color tones [illegible] ors can be changed through the inclusion complexation [illegible] ingredients from [illegible] light-induced reactions [illegible] Crystalline complexes are stable and improve [illegible] ingredients.

4 Modified Cyclodextrins

Although β-cyclodextrin forms [illegible] complexes is generally a problem. The solubility of α- and [illegible] and 23.6 g/100 ml water, respectively [illegible] perature increases, the solubility of cyclodextrins also [illegible] a guest is complexed. If the guest molecule is highly solub[illegible] more soluble than the cyclodextrin [illegible]. The polar [illegible] out of the cavity and contributes to the solubility of the [illegible] hydroxyl groups of the cyclodextrin. On the other hand, com[illegible] that is not soluble or only partially soluble in water [illegible] of the cyclodextrin. Although solubility of the complex is [illegible] it is greater than that of the guest molecule.

The solubility of cyclodextrins can be improved by [illegible] of the cyclodextrin molecule [33]. By chemical modification [illegible] very different from those of the original material. [illegible] polymer structures. [illegible] polymer can be produced [illegible] agents such as epichlorohydrin in order to obtain insolubl[illegible] ing beads. Some of these polymers retain the ability [illegible] various compounds, especially those with hydrophobic [illegible]

It has been reported that cyclodextrins are linked [illegible] produced [35]. Initial studies have shown that [illegible] hexamethylene diisocyanate. If the [illegible] piece of polymer, [illegible] within the matrix become insoluble. The chemical structure [illegible] Amaizo is shown in Figure 3.

5 Sucrose

As the most commonly used ingredient in the food industry [illegible] pyranoside) provides sweetness and is used as a bulking agent [illegible] fermentation substrate in food applications [36]. Sucrose [illegible] ent encapsulation because of the following properties [illegible] solution, (b) heat stability, (c) nonhygroscopicity, (d) [illegible] and (e) inexpensive nature [37].

In extrusion processing, sucrose and other mono- and [illegible] energy, texture, stabilization, water activity control, and [illegible] mixtures are the most commonly used coatings for extrusion [illegible] [15] reported that retention of volatiles by carbohydrates [illegible] order of sucrose > maltose > lactose > glucose > dextran [illegible] as well as the structure of the volatile influenced the [illegible]

Sucrose is used for encapsulating food flavors by a pro[illegible] 44]. However, [illegible] its chemical structure [illegible] fect crystal to that of a [illegible] size [illegible] agglomerated [illegible] modified structure has an increased void space and surface [illegible] for the incorporation of [illegible] ingredients.

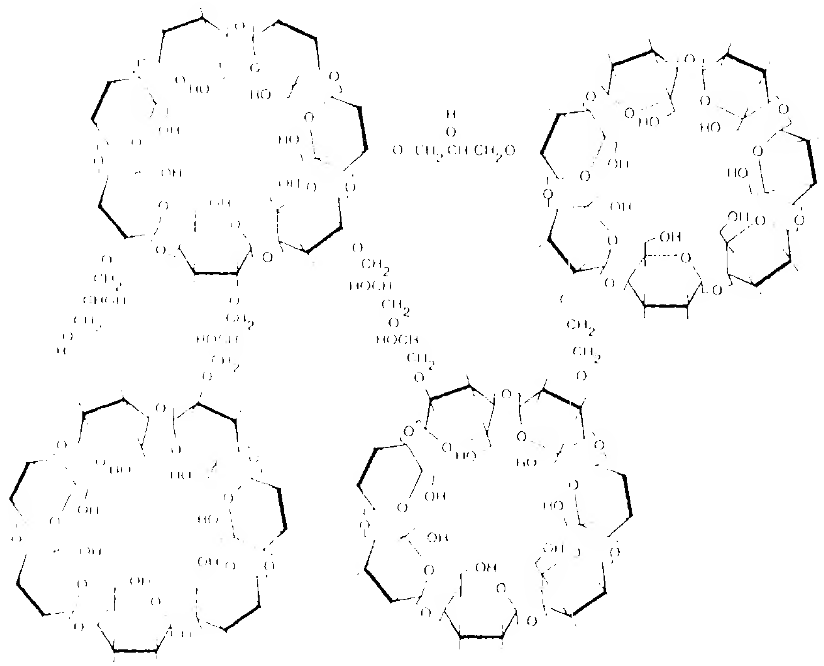


Figure 4 Structure of a polymeric, modified β-cyclodextrin. (From Ref. 30.)

6 Chitosan

Chitosan is the principal product from the alkaline hydrolysis of chitin, a main constituent of the exoskeleton of crustaceans such as crab. It consists of 2-deoxy-2-aminoglucopyranosyl residues joined by β-(1→4) linkages. Complex coacervate capsule formation can occur between chitosan, a cationic polyglucosamine, and carrageenan or alginic acid, which are anionic in nature.

Gel bead formation can be achieved by interaction of chitosans with low molecular counterions such as polyphosphates. The gelling properties of chitosans allow for a wide range of applications, the most attractive being coating of foods and pharmaceuticals and gel entrapment of biochemicals, plant embryos and whole cells, microorganisms, or algae [45,46]. Such entrapment offers diverse uses including microencapsulation and controlled release of flavors, nutrients, or drugs. Because chitosan has been shown to be an effective agent, concurrent cell permeabilization and immobilization using chitosan-containing complexes in coacervate capsules have been explored [45,46].

Polycationic chitosan molecules can be incorporated with oppositely charged polymers to form coacervate capsules of good mechanical strength. The permeability of these coacervate capsules can be controlled by altering either the type of chitosan and/or the counterion [47].

7 Cellulose

Cellulose is the main constituent of plant cell walls. It consists of glucopyranosyl residues joined by β-(1→4) linkages. Together with some other nonstarch polysaccharides, cellulose constitutes the indigest-

ible carbohydrate fraction of plant foods, referred to as dietary fi-
ber in human nutrition appears to be mainly the maintenance of no

Cellulose as an edible film for food preservation and other fo
cessing has attracted much research interest [48–50]. As an edible fi
ability of cellulose coatings can be modified by combining them w
It was found that methyl- and hydroxypropyl methylcellulose mixed
arachidic acids significantly lowered the permeation rate relative to
no fatty acids [52]. Cellulose has always been used in encapsulati
ents such as sweeteners and acids. Furthermore, it can be used to en

B. Gums

One class of material often exploited for its encapsulating capabiliti
monly, gums. These compounds are long-chain polymers that dissol
thickening or viscosity-building effect [54]. Gums are generally used
secondary effects include encapsulation [55], stabilization of emuls
control of crystallization, and inhibition of syneresis (i.e., the releas
) [56,57]. Additionally, several gums are capable of forming gels.

Food gums are obtained from a variety of sources. Although m
materials such as seaweed, seeds, and tree exudates, others are pro
and still others are produced by chemical modification of natural po
monly used as coating materials for food ingredient encapsulation

1 Seaweed Extracts

Alginates, agar, and carrageenan are extracts from red (*Rhodophyce*
algae, collectively referred to as seaweeds [58]. Their use in encap
mented. The major source of alginates used for industrial productio
pyrifera). Algae are extracted from alkali from seaweed, and the po
tated from the extract by addition of acids or calcium salts.

Alginates include a variety of products made up of β-D-mann
joined by α-(1→4) linkages. They are arranged either in regions co
other, referred to as M-blocks and G-blocks, or in regions where th
the ratio of mannuronic to guluronic acid and the structure of the p
properties of the alginate. Alginates are powerful thickening, stabiliz
are utilized in a variety of foods. At a level of 0.25–0.5%, they impro
of fillings for baked products, salad dressings, and milk chocolate and
ice crystals in ice cream during storage. They are also used as an en
reported that water-soluble alginate was capable of forming encapsu
cous high-fat food can also be encapsulated with calcium alginate fo

Agar is a heterogeneous complex mixture of related polysacchar
chain structure. Its main components are β-D-galactopyranose (galac
lactose, which alternate through 1-4 and 1-3 linkages. The chains are
sulfuric acid. Deemed as one of the most potent gel-forming agents, a
tion at concentrations as low as 0.04%. The gelling properties of the
gels, and the differential between the gel-forming and melting temper
for selecting agar. Chlorella gar has been used for the encapsulation

Carrageenan is composed of β-D-galactose and 3,6-anhydro-
sulfated as 2-, 4-, and 6-sulfates and 2,6-disulfates. The galactose resid
1-3 and 1-4 linkages. Carrageenan utilization in food processing is ba
mer to gel, to increase solution viscosity, and to stabilize emulsions and
carrageenan are thermoreversible. Because of its reactivity with certai
use at low concentrations (typically 0.01–0.03%) in a number of foo

[illegible] capsules containing meat soup or juice with agar agar, carrageenan, or pectin coatings has been developed [illegible] [67].

2 Exudate Gums

Gum arabic (acacia), gum ghatti, gum karaya, and gum tragacanth are referred to as exudate gums. Among these, gum arabic, which is a natural vegetable colloid obtained by exudation from the trunk and branches of leguminous plants of the Acacia family, primarily *Acacia senegal*, is the most commonly used encapsulation coating material [63,64]. Although there are several hundred species of Acacia, only a few are gum products, and these are located in the subdesert region of Africa.

Gum acacia is a mixture of closely related polysaccharides, with an average molecular weight range of 260–1160 kDa. Gum acacia primarily consists of D-glucuronic acid, L-rhamnose, D-galactose, and L-arabinose, with about 5% protein. This protein fraction is responsible for the emulsification properties of the gum. The gum also exists as a mixed salt of sodium, calcium, magnesium, and potassium. Owing to the complex character of this polymer, the stereochemical organization of the molecule is not completely understood, even though the qualitative and quantitative analysis of the sugars is. A hypothetical of the structure of gum acacia is presented in Figure 5.

Gum acacia is the traditional gum of choice for flavor encapsulation via spray-drying. It is an outstanding natural emulsifier and rates well based on criteria used in evaluating a flavor carrier. Because beverage applications account for a large proportion of dry flavorings used, emulsion stability in the finished product is one of the most important criteria in carrier selection. It has the advantage of being considered natural in virtually all countries. An interesting and unique property of gum acacia is its low viscosity in aqueous solutions. Although solutions containing up to 50% gum can be prepared, the solution viscosity starts to rise steeply at concentrations of greater than 35%. Most other gums yield solutions with a high viscosity at concentrations as low as 1%. It is impossible to effectively atomize these very viscous emulsions, and thus these other gums are not especially useful as flavor encapsulants.

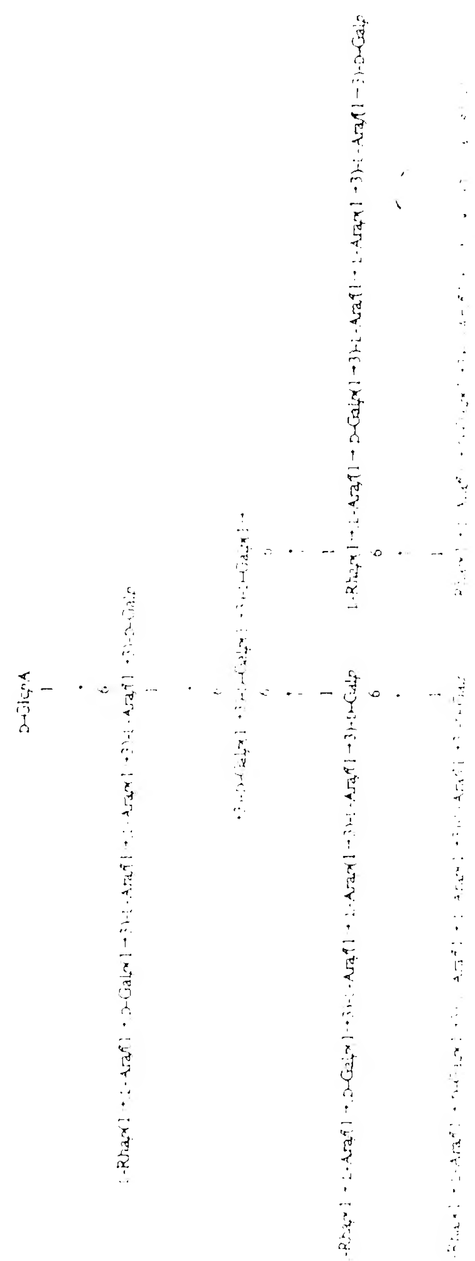
Gum acacia is also applied as a flavor fixative in the production of powdered aroma concentrates. While modified food starches are superior to traditional gum acacia in emulsion stability, gum acacia produces quite stable emulsions. The emulsions are then spray-dried. In this process, the polysaccharide forms a film surrounding the oil droplet, which then protects the oil against oxidative degradation. Compared to maltodextrins, gum acacia gives superior aroma retention during drying, and very little aroma is lost during storage at humidities below the water monolayer level [65]. New generation gums (blends of West African gums) have been shown to be superior even to modified starches for stabilizing flavor emulsions [18]. Protection of oxidizable flavorings by gum acacia varies with the source of the gum. The traditional gum acacia is not quite as good as the modified food starch–corn syrup solids blend and quite inferior to the blends of West African gums [18]. Blends of gum acacia with maltodextrins and the new West African gum acacia can be used to encapsulate flavors and offer excellent stability to oxidation [66].

C Lipids

1 Wax

Waxes are important derivatives of higher alcohols, such as C_{12}–C_{18}, which are esterified to long-chain fatty acids. Traditionally, wax coatings have been applied to fresh fruits and vegetables to extend their postharvest storage life. Edible waxes are significantly more resistant to moisture transport than most other lipid or nonlipid coatings. It has been reported that waxes are most effective in blocking moisture migration, paraffin wax being the most resistant followed by beeswax [67–69]. For this reason, waxes are commonly used as lipid coatings for encapsulation of food ingredients, particularly for the encapsulation of water-soluble ingredients. In 1980, petroleum wax was permitted for use by the FDA in formulating microcapsules for encapsulation of spice flavoring substances in frozen pizza [70].

The great resistance of paraffin and beeswax coatings to diffusion of water is related to their molecular compositions. Paraffin wax consists of a mixture of long-chain, saturated hydrocarbons,



whereas beeswax consists of 71% hydrophobic, long-chain ester compounds, 15% long-chain hydrocarbons, 8% long-chain fatty acids, and 6% other compounds [71,72]. The absence of polar groups in paraffin and the relatively low level in beeswax account for their significant resistance to moisture transport.

2 Acetoacylglycerols

Acetylation of glycerol monostearate by reaction with acetic anhydride yields 1-stearodiacetin. This acetylated monoacylglycerol displays unique characteristics of solidifying from the molten state into a flexible, waxlike solid.

It is found that the barrier properties of acetoacylglycerol improve as the degree of acetylation increases. This is due to removal of free hydroxyl groups, which would otherwise interact directly with migrating water molecules or other small polar molecules. The lower permeability through the acetoacylglycerol film prepared from technical grade monoacylglycerols might be a consequence of difference in crystal packaging or the number of free hydroxyl groups [68]. Although the water vapor permeability of acetylated monoacylglycerol films is considerably less than that of most polysaccharide films, it is greater than the permeability values of ethyl- and methylcellulose [73].

3 Lecithins

Lecithin plays a significant role as a surface-active substance in the production of emulsions. Pure lecithin is a water-in-oil (W/O) emulsifier with a hydrophile-lipophile balance (HLB) value of about 4. Because commercially used lecithins are complex mixtures of lipids, their HLB values vary considerably.

Major phospholipids of raw soya lecithin are listed in Table 3 [74]. The ethanol-insoluble fraction is suitable for stabilization of W/O emulsions and the ethanol-soluble fraction for oil-in-water (O/W) emulsions. To increase the HLB value, "hydroxylated lecithins" are prepared by controlled partial oxidation of unsaturated acyl residues with hydrogen peroxide or benzoyl peroxide [74].

Lecithin vesicles have recently been used for encapsulation of food enzymes since the formation of lecithin capsules can be achieved under relatively low temperatures. Using lecithin vesicles to encapsulate lysozyme and pepsin, it was found that the encapsulating efficiency was best when the pH was close to the isoelectric point of each enzyme [75].

Blended with other coating materials, lecithin will change the structure of microcapsules formed. Studies on the encapsulation of β-galactosidase in lecithin-cholesterol liposomes prepared by dehydration-rehydration (DR) and reverse-phase evaporation (RE) by Matsuzki et al. [76] revealed that encapsulation efficiency decreased as cholesterol content increased. A mixture of lecithin and polyethylene has been used for encapsulating other active ingredients, such as sweeteners and flavor compounds [77]. As a nutrient, lecithin has also been encapsulated as a dietary supplement [78].

4. Liposomes

A liposome (or lipid vesicle) is defined as a structure composed of lipid bilayers that encloses a number of aqueous or liquid compartments [79]. Prepared by a variety of techniques, liposomes consists of one, a few, or many concentric bilayer membranes whose size varies from about 25 nm

Table 3 Percentage of Phosphatidyl Compounds in Unfractionated and Fractionated Soy Lecithin

Type	Unfractionated	Ethanol-soluble fraction	Ethanol-insoluble fraction
Phosphatidylethanolamine	32.6	32.5	32.6
Phosphatidylcholine	32.6	65.1	4.6
Phosphatidylinositol	34.8	2.4	62.8

Source: Ref. 74.

to several µm in diameter (Fig. 6).

Over the past 20 years, liposomes have been studied extensi... ceutical areas because of their potential use as targetable carriers of ... ecules [80]. Liposome microencapsulation technologies have been ... where they can be employed in a variety of commercial applications. ... est in the use of liposomes in the food industry for development of ... characteristics, especially for encapsulation or immobilization of e...

Liposomes are prepared from phospholipids such as those fro... Semi-synthetic phospholipids with fatty acid chains of defined leng... lesterol are also used for specific purposes. The choice of the typ... of cholesterol play important roles in determining liposomal stability ... injected animals [80]. Virtually any substance, regardless of solubil... size, or other structural characteristics, can be incorporated into lipos... does not interfere with liposome formation [80]. Water-soluble ma... aqueous phase of liposomes, whereas lipid-soluble materials will be ...

Liposome structure is determined by its method of preparatio... exist for preparing liposomes [81,82], they are generally divid... multilamellar vesicles (MLV), small unilamellar vesicles (SUV) ... (LUV).

Multilamellar vesicles were first prepared by Bangham et al. ... solution of phospholipids in chloroform is evaporated producing a ... with an aqueous solution. The main advantage of MLV is that the ... be encapsulated are not subjected to harsh treatments such as exposu... intensity ultrasound. However, a major disadvantage of MLV is their ... (diameters 0.2–2.0 µm) and their low encapsulation efficiency (5– ...

Small unilamellar vesicles were first prepared from MLV by ... sound results in MLV of a much smaller size (25–50 nm in diamete... ing SUV involves injection of lipid dissolved in ethanol into the des... ing vesicles had diameters in the range of 30–110 nm, while a third ... MLV through a French pressure cell to produce liposomes with dia... [82]. The main disadvantage of SUV is their small diameter and con... ume.

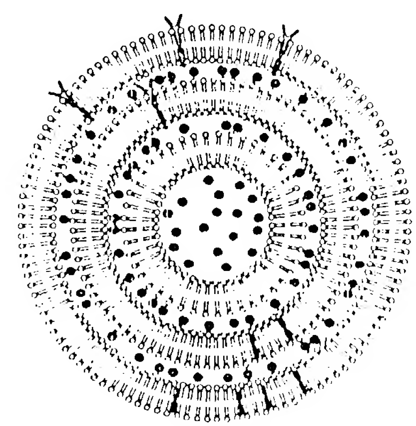


FIGURE 6 Molecular organization of a liposome. (From Ref. 1.)

Several methods are available for production of LUV whose size ranges from 100 to 500 nm; these are often the most useful liposomes. The three common methods of preparing LUV are infusion, reverse phase evaporation, and detergent dilution. In general, LUV are more homogeneous than MLV and have a higher encapsulation efficiency than SUV.

A serious drawback of the liposome preparations listed above for their application in foods has been the use of organic solvents. Liposome microencapsulation using a microfluidizer eliminates this problem because the method does not utilize any organic solvent or detergent. The two most common microencapsulation techniques, spray-drying and extrusion, encounter major problems with flavor encapsulation, the occurrence of oxidative reactions, and inability to implement procedures for intermediate moisture foods [79]. A limitation of the use of liposomes in some food applications may be their lack of stability in the presence of moderate levels of oils or hydrophobic proteins.

D. Proteins

As an important nutrient in food, proteins possess many desirable functional properties. These properties allow them to be good candidates for coating materials for the encapsulation of food ingredients. The most commonly used protein for this purpose is gelatin, even though other proteins are equally useful.

Gelatin is a water-soluble protein derived from collagen and is a valuable coating material partially because it is nontoxic, inexpensive, and commercially available. In addition to a good film-forming properties, gelatin has other ideal chemical and physicochemical characteristics that lend themselves to microencapsulation. For example, gelatin forms thermally reversible gels when warm aqueous suspensions of polypeptides are cooled. With an aqueous solution of gelatin, the change between the gel and solid state is quite definite. However, when the gelatin concentration in the aqueous solution is lower than about 1%, definite gelation cannot be observed even by cooling. These characteristic properties are effectively used for formation of capsules.

The isoelectric point of gelatin and its derivatives can be changed depending upon the method of preparation [85]. By changing the pH of the aqueous solution, either polycationic or polyanionic effects are exhibited by gelatin. This property is used for coacervation formation.

Gelatin is often used in combination with gum acacia to form coating films. Gum acacia, a hydrocolloid derived from plant sources, consists mainly of carboxylic acid functional groups. When the pH is lower than its isoelectric point, gelatin becomes polycationic, and hence there is an interaction between polycationic gelatin and polyanionic gum acacia resulting in the formation of a coacervation. As an example, if pigskin gelatin (isoelectric point pH 8–8.5) in aqueous solution is mixed with gum acacia at pH 4.0–4.5, a complex coacervation will form because of ionic attraction between the negatively charged acacia gum and the positively charged gelatin [85]. Fixing (insolubilization) of this structure can be achieved by the use of cross-linking agents such as ionized calcium. The type of gelatin and gum acacia selected and the formation and fixing procedures employed ultimately influence coating permeability [85]. Coating formation can also be achieved by a solvent-evaporation technique.

Protein-encapsulated tallow and vegetable oils have been applied to produce animal feeds [86]. Proteins can also be used, together with other coating materials, to form microcapsules. A mixture of protein and carbohydrate has been applied to an encapsulation process of oily substances [87,88].

III. MICROENCAPSULATION TECHNIQUES

A. Spray-Drying

Spray-drying is the most widely utilized encapsulation method in the food industry and is typically used for the preparation of dry, stable food additives and flavors. The process is economical, flexible in that it offers substantial variation in encapsulation matrix, adaptable to commonly used processing equipment, and produces particles of good quality [89–91]. In fact, spray-drying production costs are lower than those associated with most other methods of encapsulation. It is also one of the

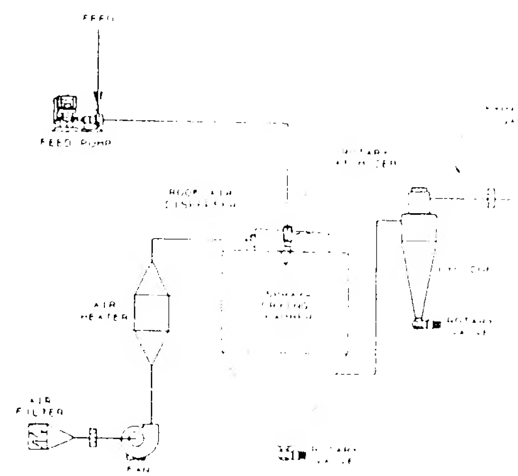


FIGURE 7 Typical spray-drying operation consisting of atomizer, air heater, fan or blower, and cyclone for proc

oldest encapsulation techniques, having been employed in the flavors using gum acacia as the coating [92].

Although spray-drying is most often considered a dehydra ration of dried materials such as powdered milk, it can be used entraps "active" materials within a protective matrix formed fr conducted in a spray dryer such as the one shown in Figure 7 an

1. Preparation of the Dispersion or Emulsion

The initial step in spray-drying an encapsulated food ingredie material or encapsulating agent. The ideal choice should have a good film former; have low viscosity at high solids levels (< 50 low hygroscopicity; release the coated ingredients when recons low in cost, bland in taste, and stable in supply; and afford goo gredients [22,93]. A food grade hydrocolloid such as a gelatin, tin, or nongelling protein [11] is generally used as an encapsul

Once a wall material or combination has been selected, it use a particular infeed solids level that is optimum for each enc chosen. Research has shown that infeed solids level is the most tention during the spray-drying process [18]. Increasing the sol ditional solids are no longer soluble benefits flavor retention by to form a high solids surface film around the drying droplets. Or 10% moisture, flavor molecules cannot diffuse through this surfa water molecules continue to do so and are lost to the drying air

A high infeed solids level means that this semipermeable assists flavor retention. It is possible to pump and atomize infee ing agent solids in excess of the solubility limits. Insoluble solid flavor molecules and therefore do not improve flavor retention d there is an optimum infeed solids level that is unique to each w

Once the encapsulating agent or mixture has been solubilized (with or without heating), the flavor or ingredient to be encapsulated is added to the mixture and then thoroughly dispersed into the system. A typical ratio of encapsulating agent to core material is 4:1, but in some applications higher flavor loads are used. Brenner et al. [100] have obtained a patent for a process that produces high load spray dried flavorings. They claim that high surface oils and poor flavor retention during drying are largely due to particle shrinkage and cracking during the dehydration process. A cracked particle surface results in substantial flavor loss during drying. Brenner et al. [100] used a combination of polysaccharides (e.g., gum arabic, starch derivatives, and dextrinized and hydrolyzed starches) and polyhydroxy compounds (e.g., sugar alcohols, lactones, monoethers, and acetals) to form an encapsulating mixture that remained plastic during spray drying. Using this plastic encapsulating agent, Brenner et al. [100] reported to have spray dried infeed materials with a flavor load of up to 75% (based on dry solids). Mass balance data showed oil recoveries of 80% at this high loading. However, higher flavor loads typically result in an unacceptable loss of flavors in the dryer. For example, Leimberger [101] has shown that compared to a 10% loading, only 33–50% of the flavor was retained during drying when a 25% flavor load was used.

2 Homogenization of the Dispersion

Prior to spray drying, the mixture is homogenized in order to create small droplets of flavor or ingredient within the encapsulating solution. The creation of a finer emulsion increases the retention of flavor during the drying process [6]. Sometimes addition of an emulsifier is required and the dispersion is then homogenized prior to spray drying. However, considerable process variation exists within the industry in this respect. Risch and Reineccius [102] reported a direct relationship between the degree of homogenization and the retention of orange peel oil during spray-drying. Therefore, it appears advantageous to efficiently homogenize the dryer infeed material. Water-soluble materials may also be encapsulated by the treatment of homogenization. Instead of having a clearly defined core and coating, the product consists of a homogeneously blended matrix of the polymer entrapping the core. These products are sometimes described as matrix particles or entrapped ingredients. They are also said to be covered with a very fine film of coating.

3 Atomization of the Infeed Emulsion

The core wall material mixture is fed into a spray-dryer where it is atomized through a nozzle or spinning wheel. The single fluid, high-pressure spray nozzle and the centrifugal wheel are two types of widely used atomizers; the industry is nearly equally divided between their use. While each type of atomizer has its advantages and disadvantages, nothing in the literature suggests that one type is superior to the other.

Atomization parameters have a significant effect upon the particle size distribution of the resultant powders. Several researchers have reported that larger particles result in improved flavor retention, but Reineccius and Coulter [16] found that particle size had no effect on flavor retention. On the other hand, studies by Chang et al. [103] indicated that there is an optimum particle size for flavor retention. Part of the controversy is cleared up by Bomben et al. [57], who showed that particle size is insignificant at high infeed solids were used. This might explain why some authors found a relationship between particle size and flavor retention while others have not. Although particle size may have a minimal influence on flavor retention during drying, it is often desirable to produce large particles to aid in dispersion upon reconstitution. Small particles are often difficult to disperse and tend to float on liquid surfaces. Larger particles can be obtained by using a large orifice, low atomization pressure (pressure nozzle only), high infeed solids, high infeed viscosity, low wheel speed (centrifugal wheel atomization only), or some type of agglomeration technique [104].

4 Dehydration of the Atomized Particles

When hot air flowing in either a co-current or countercurrent direction contacts the atomized particles, water is evaporated and a dried product consisting of starch or encapsulating matrix containing small droplets of flavor or core is formed. As the atomized particles fall through the gaseous medium, they

assume a spherical shape with the oil encased in the aqueous p
dried particles are water soluble. The rapid evaporation of wate
cation keeps the core temperature below 100°C in spite of the h
[105]. The particles' exposure to heat is in the range of a few s
advantage to this method is its ability to handle many heat labi
may contain as many as 20–30 different components (alcohols, a
boiling points ranging from 38 to 180°C, it is possible to lose
during the drying process [89]. The dried particles fall to the b
or they may be separated by a gas solid separation unit such as
ents typically have a very small particle size (generally < 100 μm
but may present separation problems in dry blends. Separation ca
by a separate agglomeration step in which the encapsulated parti
their cohesion and form large particles. Factors such as coating
of the spray dried microcapsules [106].

B. Spray-Cooling and Spray Chilling

Spray-cooling and spray-chilling are two encapsulation processe
that both involve dispersing the core material into a liquefied coa
heated nozzles into a controlled environment [107]. However, r
ter to be evaporated. Other principal differences between these p
temperature of the air used in the drying chamber and in the typ
employs hot air to volatilize the solvent from a coating disper
spray chilling use air cooled to ambient or refrigerated temperatu
atomized into the chilled air, which causes the wall to solidify a

Microcapsules produced by spray chilling and spray coolin
lipid coating. Consequently, these techniques tend to be utilized f
materials such as minerals, water soluble vitamins, enzymes, aci

In spray cooling, the coating substance is typically some
tives. However, a wide variety of other encapsulating materials m
fat and stearin with melting points of 45–122°C as well as har
melting points of 45–65°C. Taylor [89] indicated that mono- and d
of the encapsulate in the finished, reconstituted food products and
the overall emulsification system.

In spray-chilling, the coating is typically a fractionated or h
melting point in the range of 32–42°C. Coating materials with ever
but their end products may require specialized handling and storag
spray-chilling there is no mass transfer (i.e., evaporation from the
these solidify into almost perfect spheres to give free-flowing pow
an enormous surface area and an immediate as well as intimate
cooling medium.

Spray-chilling is used primarily for the encapsulation of s
sulfate, acidulants, vitamins, and solid flavors, as well as for heat s
not soluble in typical solvents [89]. Liquids may also be encapsula
a solid form, perhaps by freezing. The end product of the process, r
particle size, are water soluble but release their contents at or aro
material. With the ability to select the melting point of the wall, th
used for controlled release. The process is therefore suitable for p
terials, such as spray-dried flavors, which may otherwise be volat
mal processing. Spray chilled products have applications in baker
foods containing high levels of fat [92].

Lamb [108] pointed out the importance of maintaining optim
ing, as this can affect the fat's polymorphism, a phenomenon that

to exist in more than one crystalline form. He also noted that if a fat, for example, a powdered triacylglycerol, is permitted to exit from a chiller at too high a temperature, heat generated by polymorphism tended to reverse the encapsulating process and return the powder to a melt or perhaps a pasty mass.

C. Fluidized Bed Coating

Fluidized bed coating, also referred to as air suspension coating or the Wurster process, is a common technique used for commercial production of encapsulated ingredients for the food industry. In general, it has been found that dense particles with a narrow particle size distribution and good flowability are most suitable for encapsulation by fluid bed. Ideally a particle size distribution between 50 and 500 μm is best, although it is possible to encapsulate particles ranging from 35 to 5000 μm [8].

Solid particles to be sprayed are suspended in an upward-moving column of air in a fluidized bed chamber at a controlled temperature and humidity. Depending upon the specific application, the air flow may be heated or cooled [107]. Once the moving fluid bed of particles has reached the prescribed temperature, the encapsulation coating material is introduced to the system. Great variations in available wall materials exist. Cellulose derivatives, dextrins, emulsifiers, lipids, protein derivatives, and starch derivatives are examples of typical coating systems, and they may be used in a molten state or dissolved in an evaporable solvent. The coating is atomized through spray nozzles at the top of the chamber, whose droplets are of smaller size than the substrate being coated. The atomized particles travel down into the particle stream and deposit as a thin layer on the surface of suspended core material. The turbulence of the air column is sufficient to keep the coated particles suspended, allowing them to tumble and become uniformly coated. Upon reaching the top of the air stream, the particles move into the outer, downward-moving column of air, which returns them to the fluidized bed with their coating nearly dried (Fig. 8). The particles pass through the coating cycle many times per minute [10]. With each successive pass, the random orientation of the particles further ensures their uniform coating. In the case of hot melts, the coating is hardened by solidification in cool air. In the case of solvent-based coatings, the coating is hardened by evaporation of the solvent in hot air. The amount of coating applied can be regulated by controlling the length of time (i.e., residence time)

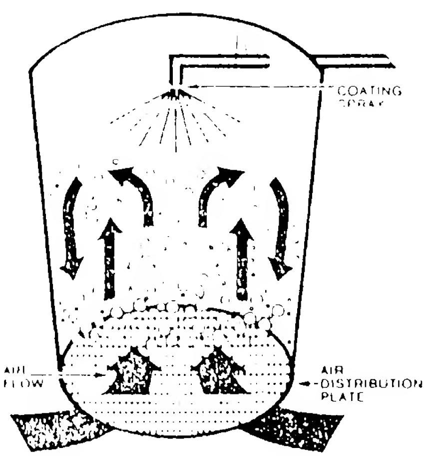


FIGURE 8 Schematic representation of a conventional air suspension system. (From Ref. 123.)

that the particles are in the chamber. In order to achieve a po
anywhere from 2–12 hours to complete. After this period,
uncoated.

D. Extrusion

Encapsulation of food ingredients by extrusion is a relatively
Extrusion used in this context is not the same as extrusion used
based products. Actually, extrusion, as applied to flavor encap
ture entrapping method, which involves forcing a core mater
mass through a series of dies into a bath of dehydrating liquid
ployed are typically <100 psi and seldom exceed 115°C, res
liquid, the coating material, which forms the encapsulating
material. Isopropyl alcohol is the most common liquid used t
cess. The extruded filaments or strands are broken into small
ity (an anticaking agent such as calcium triphosphate can faci

Schultz et al. [109] were pioneers in the extrusion encap
ange peel oil in a molten dextrose mass, poured it on stainless
verized product exhibited good stability and flavor retention o
basic formulation of Schultz et al. [109] with extrusion. Swish
ing process that is similar to the one currently used today in the
claimed in his patent [111] was the maintenance of fresh fla
otherwise would readily oxidize and yield objectionable off-fla
accelerated shelf life test on encapsulated orange peel oil that co
its shelf life was about one year. Figure 9 shows the key steps

Swisher [111] added an essential oil such as orange peel
dispersing agent, to an aqueous melt of core syrup solids (42 DE
contained from 3 to 8.5% moisture and was held at a temperat
cally 120°C. The flavor/core syrup mixture was agitated vigor
to form an oxygen-free emulsion. This emulsion was forced thr
uid (e.g., vegetable or mineral oil), which was then rapidly coole
to solidify. The hardened pellets or solid globules were ground t
isopropanol to remove surface oil, and then dried under vacu
material containing 8–10% flavoring.

The extrusion process of encapsulation has remained larg
[111]. Most research developments to date concern the compo
encapsulating matrix. For example, Beck [112] replaced the hy
bination of sucrose and maltodextrin, a melt consisting of about
(10–13 DE). Even though the low DE maltodextrin/sucrose matri
than that used by Swisher [110,111], Beck continued to emplo
ommended pyrogenic silica rather than tricalcium phosphate. Th
ranged from 8 to 10%, with 12% considered as a practical max

Barnes and Steinke [113] were awarded a patent for develo
of sucrose in a similar process. Because chemically modified st
tion properties, the authors hypothesized that an emulsifying st
ties, would absorb the flavor oil into the matrix. The maltodext
provide bulk and some viscosity control. Barnes and Steinke [1
fying starches in the encapsulation matrix would permit increa
flavoring.

Another benefit cited by the authors was that the total rep
ing starches resulted in a product that was "sugar-free." This m
keting of a final food product. Sucrose substituted with modified
ibility to manufacturers. Because sucrose will invert to glucos

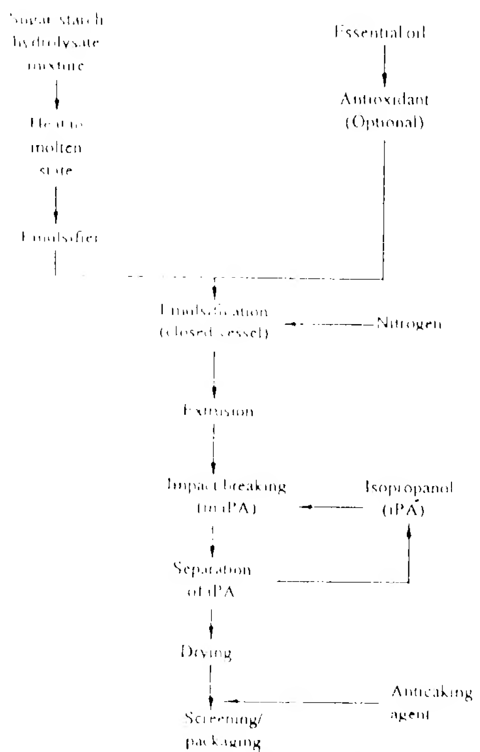


Figure 9 Flow diagram of encapsulation of food flavors via extrusion processing. (From Ref. 17.)

temperature, the resulting product would be more hygroscopic and readily participate in nonenzymatic browning reactions. Therefore, the replacement of sucrose permitted longer cooking times, larger batch sizes, and higher cooking temperatures. Barnes and Steinke [113] also claimed that fruit juices, fruit essences, volatile substances, and propylene glycol could be encapsulated in this way using their encapsulation matrix. In order to successfully encapsulate fruit essences, it was first necessary to remove water and low-molecular-weight alcohols from the essence. The essence was then incorporated into an edible oil so that it would form an emulsion with the encapsulation matrix. For example, orange juice concentrate (42% water) could be encapsulated at 10–15% loading levels with their process. This was a substantial improvement considering that prior formulations using sucrose were limited to 5–6% juice solids loading and could only be used with concentrates containing <20% water.

Miller and Mutka [114,115] were awarded two patents for flavor encapsulation via extrusion. The first patent [114] involved a process for the encapsulation of orange juice solids, while the second dealt primarily with optimization of the extrusion process. It was their intent to improve the flavor load and encapsulation efficiency. A study of the effect of cooking temperature on flavor load and encapsulation efficiency indicated that high-load products (>22%) had an optimum cooking temperature of about 123°C. As shown in Table 4, temperatures above or below this value resulted in poorer encapsulation efficiencies. Since the cooking temperature is basically determined by moisture con-

Table 4 Influence of Cooking Temperature on Encapsulation Efficiency

Oil encapsulated (%)	Encapsulation efficiency (%)	Cooking temperature (°C)
20.5	63.5	118
22.9	70.9	122
21.1	65.3	126
19.3	59.8	130
19.2	59.4	134

Source: Ref. 17.

tent, Miller and Mutka [115] postulated that too little moisture r
while too much moisture hindered encapsulation. A cooking te
about 5% moisture.

From the work of Miller and Mutka [115], optimization
concentration, and pressurization of the cooking vessel resulte
ciency at high flavor loadings. Although their patent claims that
only one example with loading as high as 22.6% was cited. The
feasibility at flavor loadings from 15 to 20%, but still such leve
flavor loadings achieved in commercial applications.

The extrusion process is particularly useful for heat labi
encapsulate flavors, vitamin C, and colorants. According to Risc
sulation in that the core material is completely surrounded by t
contacts the isopropanol and the wall is hardened, all residual o
the surface. The absence of residual surface oil and the complete
factured in this manner an excellent shelf life. This technique p
be used when visible flavor pieces are desirable. The primary ad
ably its outstanding protection of the flavor against oxidation. Fo
test on encapsulated orange peel oil containing no antioxidants wa
[110]. In terms of its weaknesses, extrusion is considerably more c
process costs are estimated to be nearly double those of spray d
ing is standard for spray drying, while extrusion delivers less flav
is currently running in the 8–12% range. Finally, one must real
tive batch process. The flavorings must be able to tolerate 110–1
period of time without deterioration.

E. Centrifugal Extrusion

Centrifugal extrusion is another encapsulation technique that has b
manufacturers. A number of food-approved coating systems ha
products such as flavorings, seasonings, and vitamins. These she
alginate, carrageenan, starches, cellulose derivatives, gum acacia
ethylene glycol.

Developed by scientists in the United States, centrifugal ex
cess utilizing nozzles consisting of concentric orifices located on
ing cylinder (i.e., head) [116]. The encapsulating cylinder or head
through which coating and core materials are pumped separately t
outer surface of the device. While the core material passes through
flows through the outer tube. The entire device is attached to a r
tates around its vertical axis. As the head rotates, the core and

through the concentric orifices of the nozzles as a fluid rod of core sheathed in coating material. Centrifugal force impels the rod outward, causing it to break into tiny particles. By the action of surface tension, the coating material envelopes the core material, thus accomplishing encapsulation. The capsules are collected on a moving bed of fine-grained starch, which cushions their impact and absorbs unwanted coating moisture. Particles produced by this method have diameters ranging from 150 to 2000 μm [117].

Another extrusion-based development is a process for encapsulating water-soluble lipids as particles of 1–15 mm. In this process, a core material is fed down a vertical tube while the coating material, an aqueous solution of sodium alginate, simultaneously flows through a ring-shaped opening around the base of the tube, forming a membrane across the bottom of the device. The extruding core material pushes against the membrane until it eventually breaks off and carries a portion of the membrane with it. Upon spinning, the particles assume a spherical shape and become encapsulated. Passage through a bath of aqueous calcium acetate, calcium glutamate, or calcium lactate finishes this film-forming process by converting the coating to a water-insoluble calcium salt.

F. Lyophilization

Lyophilization or freeze drying is a process used for the dehydration of almost all heat-sensitive materials and aromas. It has been used to encapsulate water-soluble essences and natural aromas [118,119] as well as drugs [120]. Except for the long dehydration period required (commonly 20 hours), freeze drying is a simple technique, which is particularly suitable for the encapsulation of aromatic materials.

Because the entire dehydration process is carried out at low temperature and low pressure, it is believed that the process should have a high retention of volatile compounds. Model system investigations by Flupsen and coworkers [96,121] and Flink and Karel [15,122] indicated that the retention of volatile compounds during lyophilization was dependent upon the chemical nature of the system. Flavor retention increased when the molecular weight of the carbohydrate wall materials decreased and the level of total soluble solids increased (up to about 20%).

For the production of citrus aroma powders to be used as natural flavor ingredients in soft drink dry mix formulations, Kopelman et al. [118] proposed the use of a freeze-drying method. By simply dissolving a given blend of corn syrup solids and sugars (mono- and disaccharides) in an aroma solution at a 25% (w/w) level followed by lyophilization, these authors claimed that approximately 35% of the initial aroma volatiles could be retained in the optimal maltodextrin-sucrose mixture [118].

Freeze-drying methods can also be used for other encapsulation processes. For example, Kirby and Gregoriadis [120] used freeze drying in the development of a technique known as DRV (dehydration-rehydration vesicles) for liposome entrapment. Upon the controlled addition of water, up to 20% of the water-soluble drugs present were entrapped in the formed liposomes. It has been reported that preparation of coatings only entrapped drugs that could be freeze-dried again and the liposomal structural integrity was apparently preserved. Intact liposomes with most of their contents still entrapped were obtained upon rehydration [80].

G. Coacervation

Coacervation, also called phase separation, was developed and patented in the 1950s by the National Cash Register Company in the United States and was used as a means of producing a two-component ink system for carbonless copy papers. Because of the very small particle size attainable with this process (ranging from a few submicrometers to 6 mm), coacervation is regarded by many as the original and true microencapsulation technique [123].

Coacervation involves the separation of a liquid phase of coating material from a polymeric solution followed by the coating of that phase as a uniform layer around suspended core particles. The coating is then solidified. In general, the batch-type coacervation processes consist of three steps, as summarized below, and are carried out under continuous agitation [9].

1. Formation of a Three Immiscible-Chemical P

In the first step, a three-phase system consisting of a liquid
material phase, and a coating material phase is formed by eith
tion technique. In the direct addition approach, the coating m
solutions, and insoluble liquid polymers are added directly to the
vided that it is immiscible with the other two phases and is cap
separation technique, a monomer is dissolved in the liquid vehi
ized at the interface.

2. Deposition of the Coating

Deposition of the liquid polymer coating around the core ma
physical mixing of the coating material (while liquid) and the
vehicle. Deposition of the liquid polymer coating around the co
sorbed at the interface formed between the core material and th
phenomenon is a prerequisite to effective coating. Continued de
by a reduction in the total free interfacial energy of the system
coating material surface area during coalescence of the liquid p

3. Solidification of the Coating

Solidification of the coating is achieved by thermal, cross-linking
forms a self-sustaining microcapsule entity. The microcapsules a
centrifugation, washed with an appropriate solvent, and subsequ
such as spray or fluidized bed drying to yield free-flowing, disc

Simple coacervation deals with systems containing only
while complex coacervation deals with systems containing more th
acacia [124] or gelatin and polysaccharide [125]). Coacervation in
ous phase separation and aqueous phase separation techniques.

Aqueous phase separation has been used to encapsulate en
A. It requires a hydrophilic coating, such as gelatin or gelatin-gu
particles. The resulting microcapsules may contain payloads of
tents by pressure, hot water, or chemical reaction. For nonaqueo
usually hydrophobic and the core may be water soluble or water
investigated for the encapsulation of solid food additives such as

Coacervation is a very efficient but expensive process. It ha
capsulation [7,126] because of the high costs associated with the
tered with the level of flavor that can be incorporated into the
cited by various industries for the limited use of coacervation is
suitable encapsulating materials that are food approved. Accordi
is limited primarily to encapsulated ink systems used in carbonles
fragrances that are applied in the form of "scratch-and-sniff" str
ever, work is currently in progress on this technology, and it ma
the future [127,128].

H. Centrifugal Suspension Separation

Centrifugal suspension separation is a more recent microencapsula
patented [129,130] and was first applied commercially in Februar
Europe. The process in principle involves suspending core particle
terial, and then pouring the suspension over a rotating disk appara
cess liquid between the core particles spreads into a film thinner th
excess liquid is atomized into tiny droplets, separated from the coat

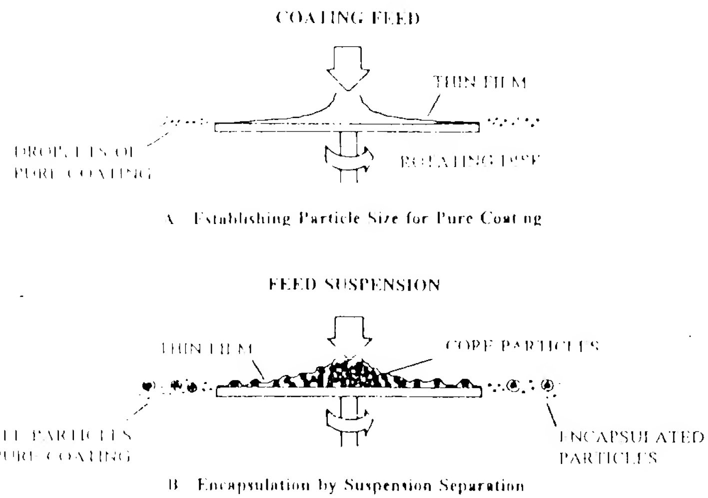


FIGURE 10 Representation of rotational suspension separation system. (From Ref. 129.)

particles leave the disk with residual liquid still around them, which forms the coating. The particles are hardened by chilling and drying [131]. The principle behind this process is illustrated in Figure 10.

Centrifugal suspension separation is a continuous, high capacity process that takes seconds to minutes to coat core particles. The process can handle a wide variety of core materials, including those that are temperature sensitive, and coating materials in solid, liquid, or suspension states without presenting aggregation problems. Furthermore, the process handles each particle only once and under most conditions produces no uncoated particles. The process has been used successfully to coat particles ranging from 30 μm to 2 mm. Coatings have been produced with thicknesses ranging from 1 to 200 μm. Macrocapsules have been prepared with payloads ranging from 1 to 97%, depending on the diameter size of the particle. Another advantage associated with centrifugal suspension separation is that the size distribution of the encapsulated particles resembles that of the uncoated particles.

I Cocrystallization

Cocrystallization is a new encapsulation process utilizing sucrose as a matrix for the incorporation of core materials. Although granulated sugar is composed of solid, dense, monoclinic spherical crystals with a limited surface area, it is not suitable as an encapsulating agent for flavor encapsulation. In order for flavors to be incorporated into the matrix, the structure of sucrose must be modified from a single perfect crystal to a microsized, irregular, agglomerated form to increase void space and surface area [37,132]. It involves spontaneous crystallization, which produces aggregates of micro- or fondant size crystals ranging from 3 to 30 μm while causing the inclusion of entrapment of all nonsucrose materials within or between sucrose crystals [133]. Use of the cocrystallization process allows many types of food ingredients—either single ingredients or combinations of ingredients—to be incorporated permanently into a crystalline sucrose aggregate, thus providing interesting and useful characteristics.

Sucrose syrup is concentrated to the supersaturated state and maintained at a temperature high enough to prevent crystallization. A predetermined amount of core material is then added to the con-

centrated syrup with vigorous mechanical agitation, thus pro... dient mixture to crystallize. As the syrup reaches the temper... tallization begin, a substantial amount of heat is emitted. Ag... and extend transformation crystallization until the agglomera... encapsulated products are then dried to the desired moisture ... size [43,44]. It is very important to properly control the rates ... as the thermal balance during the various phases. ... cocrystallized flavor are presented in Figure 11.

The agglomerates form a loose network, bonded togeth... materials are located primarily in the interstices between cry... erates, it is easy for an aqueous solution to rapidly penetrate... materials for dispersion and/or dissolution.

The cocrystallization process offers several advantage... achieve particle drying. In the highly saturated solution, nucl... rapid rate and the resulting heat of crystallization can be used to... ration. By means of the cocrystallization process, core mater... to a dry powdered form without additional drying. Because ... trenched in the modified sucrose matrix, there is no tendency...

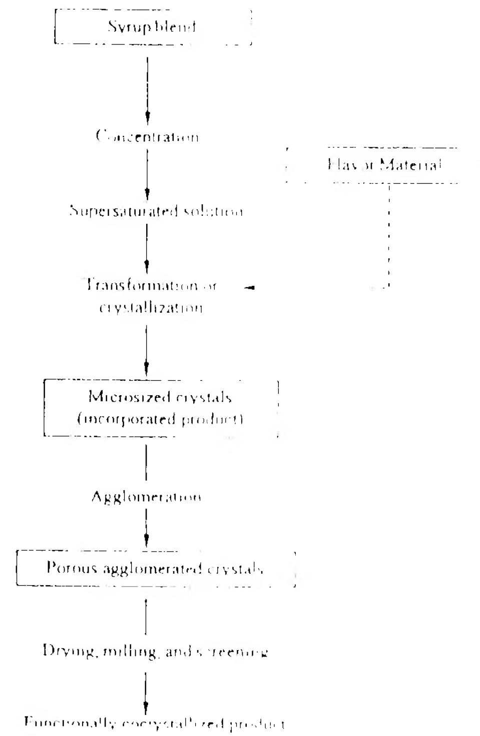


FIGURE 11 Essential steps for the preparation of a cocry...

settle out during handling, packaging, or storage. Additionally, all cocrystallized sugar/flavor products offer direct tableting characteristics because of their agglomerated structure and thus offer significant advantages to the candy and pharmaceutical industries [134].

J. Liposome Entrapment

Numerous methods of liposome entrapment have been developed [79,80,135]. Preparations obtained vary widely in vesicle size distribution, number of bilayers per vesicle, and encapsulation efficiency.

Liposomes consist of an aqueous phase that is completely surrounded by a phospholipid-based membrane. When phospholipids, such as lecithin, are dispersed in an aqueous phase, the liposomes form spontaneously. One can have either aqueous or lipid-soluble material enclosed in the liposome. However, liposome entrapment for many flavor compounds is not possible because liposomes will not form for materials that are soluble in both the aqueous and lipid phases [5]. From a physicochemical point of view, the formation of liposome structures may be illustrated by phase diagrams. A simplified phase diagram of the 1,2-dipalmitoyl phosphatidylcholine–water system is shown in Figure 12 [136]. Addition of water decreases the transition temperature of the phospholipid to a limiting value (T_c), which is the minimum temperature required for water to penetrate between the layers of lipid molecules. When the system is cooled below T_c, the hydrocarbon chains adopt an ordered packing. The structure of this phase, known as the gel, is lamellar and the hydrocarbon chains extended [136]. Each type of phospholipid molecule is characterized by a phase-transition temperature. Below T_c, its fatty acyl chains are in a quasi-crystalline array, while above T_c, the chains are in a fluidlike state.

There are two principal requirements for liposome microencapsulation. First, the lipid of choice must have a negative Gibb's free energy value (ΔG) for bilayer structure formation, because a negative ΔG value between two states of system indicates a favorable reaction. Second, sufficient energy must be put into the system to overcome the energy barrier. Close to room temperature, the value of ΔG for the formation of liposomes is always negative and, therefore, favorable. Even though thermodynamics are favorable, this does not mean that the reaction will proceed automatically; it is usually necessary to overcome an energy barrier in order to initiate a reaction. Different lipids and types of

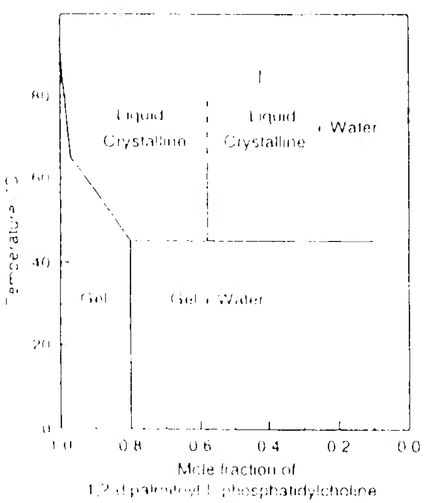


Figure 12 Phase diagram of the 1,2-dipalmitoyl-L-phosphatidylcholine-water system. (From Ref. 12.)

energy input may be used to produce different varieties of lip
methods commonly employed are described below.

1. Microfluidization

The microfluidization technique is based on the dynamic in spe
resulting momentum and turbulence allows the lipid emulsion t
An air-driven microfluidizer operates at pressures of up to 10,00
air is used to pump the aqueous emulsion of lipids, and the simpl
ized ones. The two flows interact with one another at ultrahig
microchannels.

Mayhew and Lazo [137,138] found that small (0.1 μm m
ute-capture efficiency could be easily formed by microfluidiz
concentration of 300 mM, up to 75% of cytosine arabinoside w
these liposomes. Advantages of microfluidization include: (a)
formed in a continuous and reproducible manner, (b) the avera
justed, (c) very high capture efficiencies (>75%) can be obtaine
are not exposed to sonication, detergents, or organic solvents, an
to be stable and do not aggregate or fuse.

2. Ultrasonication

Ultrasonic dispersion is often used for the preparation of SU
energy barrier through ultrasound absorption. In one approach,
mersing a metal probe directly into a suspension of large lipos
dispersion is sealed in a glass vial, which is then suspended in an
cation requires longer periods (up to 2 hours) than probe sonicat
the advantage that it can be carried out in a closed container u
contaminate the lipid with metal from the probe tip [82].

3. Reverse-Phase Evaporation

This technique has been developed for the preparation of LU
nonpolar solvents form inverted micelles (i.e., the lipid tails are
the head groups surround water droplets). When the nonpolar so
tion under vacuum, the gel-like intermediate phase changes into
vesicles. This procedure produces liposomes of quite uniform
diameter, with high encapsulation efficiency of up to 65% in low
disadvantage is that components are exposed to both organic so
sult in the denaturation of proteins and other molecules of simil

K. Interfacial Polymerization

Interfacial polymerization happens when two different polymeric
two reactive polymeric species, each solubilized in a different
one liquid is dispersed in the other. The polymerization react
the two polymeric liquids.

The interfacial polymerization process can be used to enc
hydrophobic materials. It can also be used to encapsulate aqueous
philic substances. In the interfacial polymerization microencapsula
continuous phases serve as a source of reactive polymeric species
ization reaction proceeds at a rapid rate that results in the formatio
property characteristics of a semipermeable membrane. Properties
by the reaction time [139].

The ultimate capsule size of interfacial polymerization is
monomer. In general, the capsule size ranges from about 3 μm t

size is a direct function of the agitation rate [139]. It is found that an increase in the concentration of the emulsifier yields a narrow size distribution range and a reduction of the average particle size. The patent application for the microencapsulation process utilizing the principle of interfacial polymerization was filed by IBM (serial No. 813,425) in 1959 [139]. However, use of interfacial polymerization for food systems is limited since most coatings are not food grade.

L. Inclusion Complexation—Molecular Inclusion

Molecular inclusion is another means of achieving encapsulation. Unlike other processes discussed to this point, this technique takes place at a molecular level, and β-cyclodextrin is typically used as the encapsulating medium [24]. As previously noted, β-cyclodextrin is a cyclic glucose oligomer, consisting of seven β-D-glucopyranose units linked by α-(1→4) bonds. Due to its molecular structure, β-cyclodextrin has limited solubility, a hydrophobic center, and a relatively hydrophilic outer surface, all of which affect the compound's formation of complexes.

The β-cyclodextrin molecule forms inclusion complexes with compounds that can fit dimensionally into its central cavity. These complexes are formed in a reaction that takes place only in the presence of water. Molecules that are less polar than water (i.e., most flavor substances) and have suitable molecular dimensions to fit inside the cyclodextrin interior can be incorporated into the molecule. In aqueous solution, the slightly nonpolar cyclodextrin interior is occupied by water molecules. This situation is energetically unfavorable, and therefore the sites occupied by water are readily substituted by the less polar guest molecules. Cyclodextrin complexes are relatively stable and their solubility in aqueous solutions is reduced compared to the uncomplexed cyclodextrin. Therefore, the complexed cyclodextrins readily precipitate out of solution and can be recovered simply by filtration.

The complexing of a cyclodextrin with a guest compound can be accomplished by three methods [33]:

1. Stirring or shaking the cyclodextrin and guest molecules to form a complex, which could then be easily filtered and dried. In some cases, complexation of an insoluble guest can only be accomplished through dissolution of the guest in a water-soluble solvent.
2. Blending of solid β-cyclodextrin and guest with water to form a paste. Solvent should not be used. This method is particularly applicable for oleoresins.
3. Forcing a gas through the solution for complexation to occur. This method is seldom used.

It should be emphasized that there are several variations to these basic techniques, but in all methods both the cyclodextrin and the guest molecules must be solubilized. If the guest material is insoluble in water, it is necessary to dissolve it in another solvent such as alcohol.

The composition of the cyclodextrin complex formed depends greatly upon the molecular weight of the guest molecule in question. Because one molecule of cyclodextrin will normally include only one guest molecule, the loading depends upon the compounds included. It should be noted that the theoretical maximum loading is not always obtained. For example, Pagington [140] stated that dimethyl sulfide could be complexed at 5.5%, but only 2% loading has been observed.

It has been reported that cyclodextrins have a variable affinity for different guest compounds. This may be used to advantage or it can be disadvantageous. Some researchers have made use of the variable binding properties offered by β-cyclodextrin to selectively remove bitter compounds from orange and grapefruit juices [141]. Variable binding properties can also be a disadvantage when it comes to the encapsulation of flavor compounds. Reineccius and Risch [24] formed zero (isoeugenol) to 100% inclusions (ethyl hexanoate and linalool) when they added a model flavor system to β-cyclodextrin in an ethanol-water mixture. The losses of flavor compounds were due to the lack of inclusion rather than a loss during the subsequent complex recovery and/or drying steps. Once the complex was formed, it was quite stable to evaporation.

The variable inclusion properties of cyclodextrins wou
from that of the original flavor when the flavor is comprised of a
an artificial flavor that contains short chain esters and longer
However, flavors such as orange which have been included in β
able from fresh orange even by trained taste panels [142].

There are substantial data in the literature that document
treated with cyclodextrins [7,142–144]. As previously mentio
formed is very stable to evaporation. Szente and Szejtli [144]
cluded volatiles after 2 years of storage at room temperature. T
dative stability of the included guest compounds. Many repor
complexes are quite stable to oxidation [142,144].

As with all processes, there are limits to the application
formation of flavors [145]:

1. There is a limited amount of flavor content in
weight).
2. The size and polarity of flavors to be complexed li
3. Cyclodextrin can act as an artificial enzyme, someti
sis of some ester-type flavor components. This can
of the flavor.
4. The water solubility of β-cyclodextrin flavor comp
that of spray dried and other microencapsulated s

IV. ENCAPSULATED INGREDIENTS AND THEIR A

Microencapsulation can potentially offer numerous benefits to
Various properties of active materials may be changed by encaps
flow properties can be improved by converting a liquid to a soli
materials can be protected from moisture, and the stability of ingr
light, or oxidation can be protected, thereby extending their shelf
incompatible can be mixed and used safely together. Currently
microcapsules being utilized as food additives in North America
below.

A. Acidulants

Acidulants are added to foods for a variety of reasons. They can b
vation aids, and processing aids. In addition, they facilitate the
textural effects in foods because of their interaction with other in
proteins, starches, pectins, and gums [146].

Unencapsulated food acids can react with food ingredients to
These include decreased shelf life of citrus-flavored and starch co
pie fillings in which the acid hydrolyzes the starch), loss of flavor,
tion of ingredients. Encapsulated food acids overcome these probl
clude oxidation and provide controlled release under specific conditi
reduce hygroscopicity, reduce dusting, and provide a high degree

Encapsulation of acids in a time-release matrix is suggested
able reactions of acidulants with other food ingredients. The mate
lating coat in the acid products is generally a partially hydrog
maltodextrin and emulsifiers are also available for this purpose. T
leased at the appropriate time in the processing operation either by
coating material or by contact with water or a combination of these
encapsulated acidulants are given below.

1. Meat Processing Aids

In the meat industry, encapsulated acids, such as lactic, citric, and glucono-δ-lactone (GDL), are used to assist in the development of color and flavor in meat emulsions, dry sausage products, uncooked processed meats, and meat-containing products, such as pasta meals. Fat encapsulation allows the acid to survive the blending process, giving a uniform dispersion within the meat. Later, the encapsulated acid controls the drop in pH and prevents the meat from prematurely setting [8].

Cured meat products, especially dry and semi-dry sausages (e.g., summer sausages, pepperoni, hard salami), have historically been prepared using lactic acid–producing bacterial cultures to develop flavor and lower the pH. Bacteria is added to the meat emulsions and allowed to proliferate until a sufficient amount of lactic acid is generated. Upon its production, the pH drops, binding occurs, and flavor develops. However, such products often tend to have inconsistent flavor, color, and textural characteristics from batch to batch. Uncoated lactic acid and citric acid cannot be added to meat during curing because they react almost instantly with the meat, rendering it unsuitable for further processing. Contamination is especially troublesome where the meat processor may use fermented raw meat as the source of bacteria rather than frozen cultures. However, an encapsulated acid, which is formulated for delayed release under smokehouse temperatures, can be used as an alternative to the cultures. Acidification by encapsulated acids can improve emulsification and protein binding of emulsified meat and poultry products and impart the "tangy" flavor found in fermented sausages without the complicated use of lactic acid starter cultures. Encapsulation permits addition of the acidulants prior to stuffing without premature denaturation/binding of meat.

About 25 years ago, encapsulated acids in a heat-rupturable inert vehicle such as ethyl cellulose were developed [147]. The encapsulated acids were mixed with nitrite-treated ground meats, and upon thermal processing the acid was released bringing about a lowering in the pH of the meat and giving rise to rapid development and stabilization of cured meat color. The more acidic conditions of the meat assisted the production of nitrous acid or dinitrogen trioxide from the exogenous sodium nitrite. Both nitrous acid and dinitrogen trioxide are nitrosating species, which interact with the prosthetic heme group of myoglobin to form the cooked cured-meat pigment.

The effect of encapsulated food acids on restructured pork from prerigor sow meat was studied by Cordray and Huffman [148]. Results from sensory panels showed that sodium acid pyrophosphate (SAP) and encapsulated GDL treatments yielded products with a more intense flavor than that of the control sample; objective analysis revealed no difference in shear value, tensile strength, water holding capacity, cooked yield, or chilled yield. Significantly more of the total meat pigment was converted to nitrosohemochromogen in the GLD treatment than in the control sample. Lactic acid can also be encapsulated by plating it onto a particle calcium lactate carrier and then encapsulating the carrier and acid with a molten edible lipid [149].

2. Dough Conditioners

The baking industry has long been aware of the need for stable acids and baking soda for use in wet and dry mixes to control the release of carbon dioxide during processing and subsequent baking. Products commonly encapsulated for bakery applications include a variety of leavening system ingredients, as well as vitamin C, acetic acid, lactic acid, potassium sorbate, sorbic acid, calcium propionate, and sodium chloride.

Use of ascorbic acid (vitamin C) for the strengthening and conditioning of bread and roll doughs provides many positive effects to the finished products. Examples of these are stronger sidewalls, uniform crust color, and improved slicing, in addition to a stronger structure, which support the addition of other protein-rich ingredients (such as soybean flour, nonfat milk powder, and wheat germ). However, because ascorbic acid degrades rapidly in the presence of water and oxygen, most of the acid is destroyed before it is needed. Encapsulated in an edible coating, ascorbic acid imparts some of the effect of an oxidizing agent when used alone in natural breads. In combination with bromate, it enables greater amounts of protein-rich ingredients to be utilized without disturbing the grain of the bread to any great extent [150].

For yeast-raised doughs, encapsulated salt, potassium sor[illegible] because they do not allow the pH to drop too early in the baking [illegible] Once baked, however, the mold-inhibiting properties of the [illegible] [8].

3. Other Encapsulated Acidulants

Acids are frequently used as liquids but would be easier to hand[illegible] forms. Seighman [151] developed a method for encapsulation [illegible] dispersion containing a film-forming agent (hydrogen octenyl[illegible] matrix-forming ingredient (modified and hydrolyzed starches). [illegible] and then extruded into cold aqueous alcohol to solidify the matri[illegible] the film-forming agent to harden to a vitreous structure.

B. Flavoring Agents

The development and production of artificial or natural flavors ar[illegible] in the food industry. The vast majority of flavor compounds use[illegible] and constituents of the flavors tend to show sensitivity towards [illegible] temperatures. Moreover, these flavor concentrates are oily and [illegible] difficult to work with. Therefore, it is necessary to employ a pr[illegible] pounds to a more useable form. One of the purposes behind encap[illegible] conversion of liquid flavors to dry powders. Microencapsulated [illegible] a solid form over a liquid one, with reduced volatility and less [illegible] sulation has become an attractive option to transform liquid food f[illegible] ing powders, which are easier to handle and incorporate into a d[illegible]

The flavor industry depends heavily on encapsulation as a [illegible] compounds that offer them protection until consumption. Flavor[illegible] lated by a variety of processes and provides numerous advantage[illegible] flavor encapsulation and encapsulated flavorings prepared during [illegible] in Table 5.

Examples of commonly used encapsulated flavors are citr[illegible] oils, spice oleoresins, and whole spices. Citrus oils are very susc[illegible] unsaturation in their mono- and sesquiterpenoid structure. Oxida[illegible] velopment of off-flavors described as painty or turpentinelike. F[illegible] spray drying in a maltodextrin matrix, have a greater stability tha[illegible]

Because flavors are often volatile materials, the stability of [illegible] tant consideration. Microcapsules must be stable for an extended [illegible] uids can be encapsulated and subsequently dried to form free-flow[illegible] activity during storage. Table 6 illustrates the stability of encapsu[illegible] age time in microcapsules of various particle sizes under ambient [illegible]

Flavors encapsulated by inclusion complexation in β-cyclod[illegible] tilization and attack by oxidation [140,144]. Storage stability of flav[illegible] under "nonstress" conditions at room temperature showed that mole[illegible] provides an almost perfect preservation of flavors for up to 10 yea[illegible]

There has been a great expansion in the development of tec[illegible] spray-dried composition comprising a volatile and or a labile com[illegible] encapsulated in an extruded glassy matrix. Such a procedure of d[illegible] been developed by Levine et al. [191]. Excellent reviews of mi[illegible] applies to food flavors have been written [6,12,89,105,152,154,15[illegible] details about these techniques are difficult to obtain because they

Table 5 Literature on Flavor Encapsulation

Subjects	Ref.
Overall reviews	7,9,11,89,152–156
Spray drying	90,98,99,105,152,157–159
Coacervation systems synthetic film formers	153,160
Cheese flavor technology	161–166
Flavor oils	167–171
Lemon and citrus oils	172,173
Safflower oil	174
Essential oil for bakery mixes	175
Volatile flavorings (aroma)	42,126,176–180
Use of cyclodextrins	181
Use of extrusion coating	182
Use of fluidized bed by spraying	182
Use of sorbitol and other ingredients	183
Use of water insoluble coatings	55
Flavor food ingredients encapsulation	184–186
Coffee and tea flavor encapsulation	145,187,188
Seasonings	61,189
Spray dried spice oils	106
Artificial flavors	24
Flavors from microorganisms	190

Source Ref. 12

C. Sweeteners

Sweeteners are often subjected to the effects of moisture and/or temperature. Encapsulation of sweeteners, namely sugars and other nutritive or artificial sweeteners, reduces their hygroscopicity, improves their flowability, and prolongs their sweetness perception. Sugar that has been encapsulated with fat and incorporated in a chewing gum requires more shear and higher temperatures to release its sweetness than uncoated sugar, which dissolves more rapidly in the mouth.

Table 6 Stability of Microencapsulated Flavors

Encapsulated flavor	Average capsule size (μm)	Storage period (days)	Flavor content in microcapsules (%) Initial	(%) Final
Cassia	750	730	87.8	86.1
	20	730	63.1	59.2
	600	400	90.2	89.9
Lemon	250	500	70.5	76.3
	40	730	74.0	67.9
	20	730	60.1	59.9
Lime	1,000	409	92.5	89.6
Peppermint	500	732	75.3	74.6
	20	730	58.5	56.3

Source Ref. 12

Table 7 Changes in the Flavor Content of Cyclodextri
Spice Complexes after 10 Years Under Normal Storag
Conditions

Sample	Flavor content of the samples In 1977	In 1987
Garlic oil	10.2–10.4	10.0–10.3
Onion oil	10.4–10.6	10.2–10.4
Caraway oil	10.5	9.9–10.2
Thyme oil	9.4–9.8	9.0–9.2
Lemon oil	8.9–9.1	8.6–8.8
Anise oil	9.0–9.2	9.0–9.3
Peppermint	9.4–9.7	9.0–9.2
Marjoram	8.8–9.0	8.0–8.2
Orange	9.0–9.5	6.0–7.0
Tarragon	10.0–10.3	8.8–9.0
Mustard	10.8–11.0	11.0–11.2

Source Ref. 12

Patents for the encapsulation of sweeteners were award
cal development of encapsulation allowed their commercial u
is the most widely studied. Aspartame is the methyl ester of a
ids, phenylalanine and aspartic acid (aspartate). Although this
der has a very intense sweetness (approximately 180–220 time
its use in food has, in the past, been limited. At high temperature
acids aspartic acid and phenylalanine, accompanied by a loss of
keted sweetener has now been encapsulated by many methods.

Patents awarded to Cea et al. [192,193] mainly involve t
L-phenylalanine methyl ester as a chewing gum composition.
lated APM overcomes difficulties experienced in the use of AP
presence of water or elevated temperature [192,193]. Yang and
encapsulating aspartame in a film composed of high molecular w
phobic plasticizer (mono- or diacylglycerol with fatty acid
[186,194,195]. In this process, active ingredients, including sol
and drugs, can also be encapsulated. The product can be used to
life, with highly controlled release of active ingredients [186].

A process developed by Cherukuri and coworkers can b
system. It comprises a dipeptide or amino acid sweetener or flav
in a mixture of fat and high melting point polyethylene wax [1

Gas chromatographic analyses were used to measure the r
mint, and natural lemon flavors, which had been cocrystallized, a
under ambient conditions. Data indicated no significant change i
of storage. Results from oxidation studies [199] showed that pe
very good shelf life, even after storage for an appreciable period
have published a number of patents in this area. Some typical ex
cocrystallization are listed in Table 8.

D. Colorants

Natural colors such as annatto, β-carotene, and turmeric present
and may create dust clouds. Encapsulated colors are easier to ha

TABLE 8 Examples of Products Encapsulated by Cocrystallization

Flavored sugar crystals	Brown sugar, chocolate, honey, molasses, and peanut butter granules
Fruit juice crystals	Cranberry, grape, orange, raspberry, and strawberry juices
Essential oil powders	Cinnamon, lemon, orange, and peppermint oils
Dry flavors	Barbecue, beef fat, butterscotch, chocolate, maple, and smoke flavors
Volatile substances	Acetaldehyde and diacetyl

stability to oxidation, and control over stratification from dry blends. Synthetic colors, together with other food ingredients, can also be encapsulated for improving their stabilities [201].

A technique for solubilizing oily substances in micellar solutions of protein and carbohydrates was applied by Ono [202] in order to achieve encapsulation of two oil-soluble pigments - paprika oleoresin and β-carotene. The pigment in oil was solubilized in an aqueous solution containing 60% (w/w) corn syrup solids and 1% (w/w) polypeptone. The solubilized mixture obtained was solidified by vacuum drying at 60°C and formed into granules by crushing and sieving. These granules containing approximately 12% pigment-containing oil underwent virtually no discoloration during storage for 20 days at 60°C or when subjected to irradiation from a fluorescent lamp. Dispersibility of the pigments in water was improved by their encapsulation in a protein carbohydrate matrix [202].

Ciliberto and Kramer [203] developed an encapsulation process for producing granular water-soluble food ingredients, which otherwise deteriorated on exposure to the atmosphere (such as coloring agent). It was claimed that the resulting coated particles had a long shelf life and were still substantially instantaneously soluble in water.

Studies on encapsulation of preformed cooked cured-meat pigment (CCMP) showed that the CCMP may be stabilized effectively by its encapsulation in food-grade starch based wall materials. The color stability of the treated meat products was found to be similar to their nitrite-cured analog [204].

E. Lipids

Lipids contribute to more than 30% of the dietary energy of North Americans, and similar figures apply to many other affluent societies. Use of lipids/fats is commonplace in food-processing practices, but the susceptibility of lipids to oxidative degradation during processing and storage is always a concern; particular attention must be paid to foodstuffs containing higher proportions of polyunsaturated fatty acids (PUFA). One possible way to protect lipid moieties against oxidative deterioration is via encapsulation. Early research in this area was mainly focused on production of encapsulated lipids for animal feed [174,205–207], but more recently, encapsulated high-fat powders or shortenings have been available in food formulations for human consumption [208].

Because of the pro-health benefits of fish oils, encapsulated oils have been available in health food stores, pharmacies, and supermarkets for a number of years. These fish oils contain long-chain omega-3 PUFA, such as eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), and docosapentaenoic acid (DPA), whose beneficial effects have been ascribed to their ability to lower blood serum triacylglycerol and cholesterol levels [209,210]. While DHA is essential for proper functioning of the eye and may have a structural role in the brain, EPA serves as a precursor to eicosanoid compounds [211] and has therapeutic benefits in human cardiovascular diseases [212,213]. It should be noted that fish oils are exceptionally susceptible to autoxidation and can form complex mixtures of high molecular weight oxidation products. Shukla and Perkins [214] reported that because of the unknown health effects of the oxidative polymeric materials and their high level in some encapsulated oils, caution should be exercised when ingesting fish oil capsules on a regular basis. However, encapsulation can enhance the oxidative stability of these oils.

Gejl-Hansen and Flink [215] freeze dried an aqueous emu
coating in the presence of detergents. The microencapsulated
oxidative deterioration even though more effective encapsulating
Ono and Aoyama [88] reported that vacuum-dried rice bran oil e
syrup solids and pork polypeptone did not undergo much oxid
temperature for a few weeks. Taguchi et al. [216] reported the
bedded in spray-dried egg white powder and use of the produ
fortification of cookies. These authors reported that use of m
cookies did not affect their sensory quality.

The antioxidative effects of spray-dried powders at vario
coholic solutions of gliadin, linoleic acid, and palmitic acid wer
by simple mixing of these components in the same portions a
substituted for gliadin by Iwami et al. [217]. It is reported that
experiment were highly resistant to oxidative deterioration dur
[217]. Shahidi and Wanasundara [218] spray dried an emulsion
26% long-chain omega-3 fatty acids, with either β-cyclodextrin
They found that β-cyclodextrin was the most effective entrap
deterioration of seal blubber oil.

F. Vitamins and Minerals

Most vitamins cannot be synthesized by the body and must be
vitamins are such important nutritional and dietary factors, p
fortified with vitamins. Table 9 presents the recommended daily
C, B_6, B_{12}, folic acid, thiamine, riboflavin, and niacin as compil
ences' Food Nutrition Board [220]. Vitamins and minerals are
variety of foods.

Encapsulation of vitamins and minerals offers many adva
tributed by certain vitamins and minerals, permits time release o
vitamins to extremes in temperature and moisture, and reduces
ingredients. Encapsulation also improves flow properties and redu
to dry mixes. Both fat- and water-soluble vitamins may be enc
to provide many advantages. Hall and Pondell [221] developed
mineral particles. The coating matrix for this process is chiefly

TABLE 9 Recommended Dietary Allowances

Vitamin	Men	Wo
Fat-soluble		
Vitamin A (retinol, μg)	1000	8
Vitamin D (cholecalciferol, μg)	5–10	5
Vitamin E (α-tocopherol, mg)	10	
Vitamin K (μg)	45–80	45
Water-soluble		
Vitamin C (mg)	60	6
Vitamin B_1 (thiamine, mg)	1.5	1
Vitamin B_2 (riboflavin, mg)	1.7	1
Niacin (mg)	19	1
Vitamin B_6 (pyridoxine, mg)	2.0	1
Vitamin B_{12} (μg)	2.0	2
Folic acid (μg)	200	18

lene glycol monoester and acetylated monoglycerol. Vitamins and minerals can also be encapsulated in fat [222] or in starch matrices [223].

For encapsulation of water-soluble vitamins, ethyl cellulose is useful because it is water insoluble and coatings with increased thickness reduce the water permeability of the prepared capsules. Thiamine enrichment of some bakery products such as devil's food cake, ginger snaps, and soda crackers, has always been unsuccessful due to vitamin destruction in the neutral or alkaline pH. A procedure for microencapsulating thiamine in an ethyl cellulose coating to protect it from alkaline conditions experienced in bakery products and to mask its undesirable bitter taste has been developed [224].

Riboflavin, thiamine, and niacin are partially destroyed during the processing and cooking of pasta products. Studies on unprotected versus encapsulated thiamine, riboflavin, and niacin in cooked enriched spaghetti showed that concentrations of the three B vitamins tested were higher in cooked pasta that contained encapsulated vitamins [225].

Lipid soluble vitamins lose their activity due to isomerism, anhydro-vitamin formation, oxidation, and photochemical reactions [140]. Losses of vitamins in fortified foods can be minimized if they are added as cyclodextrin complexes [140] or gelatin-encapsulated beadlets [226]. It was found that the stability of vitamin A in skim milk was substantially increased by encapsulation in gelatin. Loss of the vitamin in fortified milk powder was minimal even when heated at 100°C for 9 minutes or stored at 28°C for 40 weeks [226]. Table 10 presents the stability data of vitamin A palmitate, of 325,000 units per gram potency, encapsulated in a modified gelatin film [13]. The data indicate that the rate of vitamin A degradation under the test conditions is significantly reduced by microencapsulation.

A well designed phase-separation technique for encapsulation of vitamin A has been developed by Markus and Peleh [227]. The matrix components used consisted of substituted cellulosic materials, fatty acids, or a variety of proteins. Antioxidants such as butylated hydroxytoluene and ethoxyquin were incorporated in the formulations. It has been claimed that the capsules prepared with substituted cellulosic materials protected vitamin A best from degradation [227].

Iron compounds have been encapsulated to improve the color, odor, and shelf life of fortified products. Encapsulation reduced the ability of iron to react with other food ingredients and also lightened the color of an unspecified type of electrolytic iron [228]. The process for encapsulation of ferrous sulfate was developed by Jackel and Belshaw [229] in the 1970s. It is reported that encapsulated $FeSO_4$, a fine, white, free-flowing powder, can withstand 6-month storage without any deteriorative change. Harrison et al. [230] examined the effect of iron in various forms on the oxidation of lipids in white flour. When subjected to an accelerated stability test (stored at 50°C), flours enriched with ferrous sulfate, fat enriched with ferrous sulfate, electrolytic iron powder, and carbonyl iron powder developed an unacceptable oxidized flavor after 8 days. However, oxidation was not detected in flour stored at room temperature for 2 years [230].

Soy milk beverages have gained attention as possible alternatives to cow's milk. However, soy milk is nutritionally inferior to cow's milk with respect to its calcium content. Attempts to fortify soy milk with calcium have been unsuccessful since soy protein was coagulated and precipitated by cal-

Table 10 Stability of Vitamin A Palmitate at 45°C and 75% Relative Humidity

	Percentage of potency retained	
Time (days)	Raw oil	Microcapsulated
5	86.1	98.3
15	84.2	97.8
42	76.2	94.2
56	69.9	94.1

Source: Ref. 12.

cium [231,232]. Hirotsuka et al. [232] found that calcium coated w
be added to soy milk without undesirable calcium-protein interac
in fortifying 100 g of soy milk with an additional 120 mg of ca

G. Enzymes

Enzymes are being used increasingly in the food industry for a w
sulation of enzymes could enhance their properties in a number o
foremost of these concerns is stability. The complex biochemical
it highly vulnerable to inactivation by other components or con
segregating it inside a microcapsule, it can be maintained in conc
harmful to it. A variety of other stabilizing materials can be enc
protect them from different antagonistic effects. Inhibitory agents
from the capsule. Penetrating ions can be removed by buffers or c
age may be prevented by the use of antioxidants. Thermostabilizer
extreme processing conditions such as dehydration or freezing. Fu
by simply maintaining the enzyme in a concentrated form rather
into the bulk-food phase.

As long as it remains encapsulated, the enzyme will be iso
fore latent and passive within the food matrix. By selecting a caps
can choose when, where, and how it will interact with its intended
properties of the microcapsules, they can often be made to accum
location within the food. When they eventually break down, the en
at the intended target site rather than nonspecifically dispersed
enzymes can be used much more selectively and with far greater e
would allow.

The timing of enzyme release can be controlled by selectin
stability properties within a particular food system. A low stabili
food process, whereas a more stable one will allow postponement
where early release is undesirable and enzyme action is not neede
process.

Considerable progress in research for the control of cheese rip
has been achieved [161,162,164,233–238]. Principles involved i
illustration of how encapsulation can be applied generally to the fo
by Kirby and Law [165]. Other enzymes such as lipase [239,240]
been encapsulated for applications in food processing.

H. Microorganisms

Encapsulation of viable bacterial cells has several advantages over
ripening enzymes. The stability of enzymes in intact cells is grea
production achieved by cells is easily manipulated by control
microcapsules [237].

Cells of *Brevibacterium linens* were successfully entrapped i
by Kim and Olson [238]. It is believed that the bacteria, using met
and other sulfur compounds, makes a major contribution to the C
cheese products. Microencapsulated microorganisms may be useful
blue cheese or in imparting blue cheese flavor to other foods. Spore
been encapsulated in a milk fat coating matrix [156]. The micr
microcapsules enhanced methyl ketone production by spore enzym
that there are fewer examples of encapsulated microorganisms, esp
zymes.

I Gases

Some hard candies can be made with entrapped carbon dioxide gas [239]. The confections made with encapsulated carbon dioxide produce a sizzling effect on the tongue as the candy melts in the mouth. The candy is produced by incorporating gas at a pressure of 50–1000 psi into the molten sugar. Concentrations of carbon dioxide in the candy range from 0.5 to 15 ml/g of sugar [239]. Gas can also be injected into the encapsulation system and be coated together with the foaming and aromatic core mixtures [179].

J. Other Food Additives

Almost all food additives can theoretically and technically be encapsulated. However, only some encapsulated additives are commercially available because many factors have to be taken into consideration before the process leads to commercial manufacture. Research has been done to encapsulate food preservatives such as monocapric acid [243] and oleic acid [244]. A process for preparing a coated particle salt substitute composition was described by Meyer [245]. Recent studies suggested that encapsulated antioxidants could be beneficial to food preservation [246]. It is expected that many new encapsulated food ingredients will be produced, which could contribute greatly to further development of food processing and preservation.

V CONTROLLED RELEASE MECHANISM AND EFFECTS

Encapsulation allows reactive ingredients to be separated from their environment until their release is desired. Although separation is indeed the objective of encapsulation, release mechanisms of the core material must be considered as well. In fact, when designing a custom encapsulated ingredient, one must determine the desired release mechanism and a method for quality measurement. A well-controlled release of core material is a very important property of microcapsules. For example, a substance in formulated food may be released upon consumption but prevented from diffusing throughout the product during processing operations (e.g., flavors, nutrients). Similarly an additive may be released in a specific processing step but protected in preceding operations (e.g., acids, leavening agents, cross-linking agents) [247].

Because the physical and chemical properties of volatile compounds are governed by their structure and cannot be changed, one has to manipulate the choice of the encapsulation matrix as well as the formulation of the flavor itself if the flavor is a compound one. By picking a capsule matrix with limited selectivity, which may in fact be chosen to discriminate against vapor pressure differences and the desired flux rate (to release slowly or quickly but uniformly), flavor imbalances can be minimized. Additionally, if the flavor is a formulated one, there may be some opportunity to choose flavor compounds that will have similar release rates. Such well-controlled release-delivery systems present the food technologist with exciting opportunities for improving the performance of existing food processes as well as for the development of entirely new ones [166,247]. However, in order to address the issue of controlled release, one needs to examine the basic principles of controlling the release of encapsulated materials and then consider which technologies can be applied in the food industry. The various mechanisms of release from controlled release-delivery systems in consumer products are provided in Table 11 [248].

A. Release Rate

Release rates that are achievable from a single microcapsule are generally zero, half, or first order. Zero order occurs when the core is a pure material that may be released through the wall of a microcapsule as a pure material. Half-order release generally occurs with matrix particles, while first order release occurs when the core material is actually a solution trapped within a solid matrix [247]. As the solute material releases from the capsule, a desired concentration of solute is reached.

TABLE 11 Mechanisms of Release from Controlled Re… Delivery Systems in Consumer Products

Diffusion-controlled release	Membrane controll…
Pressure activated release	Tearing or peeling r…
Solvent-activated release	Osmotically control…
pH-sensitive release	Temperature sensiti…
Melting-activated release	Hybrid release

Source: Ref. 248.

A mixture of microcapsules will include a distribution … thickness. The effect, therefore, is to produce a release rate d… because of the ensemble of microcapsules. Thus, it is desirabl… tal basis of the release rate from an ensemble of microcapsule… theory due to the distribution in size and wall thickness [1]. … rate of core materials are summarized in Table 12.

B. Release Mechanisms

The coating not only protects the core material from moisture … and additional external agents [123], but it allows/assists in co… Thus, release of the core material is dependent upon the type an… material used to form the microcapsule. These factors dictate t… sule, which may be based on solvent effects, diffusion, degrada… riety of release mechanisms that have been proposed for micr…

1. Fracturation or Pressure-Activated Release

A number of controlled release systems prepared primarily by … pressure for release of the active core [250]. The coating can b… nal forces, such as pressure, shearing, and ultrasonics, or by … microcapsule having a permeation-selective coating. Both fr… controlled release of soluble materials; however, a slow releas… the case of fracturation is a detriment rather than an attribute. A… needed that releases only on rupture. For example, capsules m… insoluble in water but can be made to release their contents by … by increasing the temperature to the melting point of the fat (s… the most commonly used mechanical release means. It is also p… stance by incorporation of a swelling agent into the core substan… using discharge or magnetic force. The force fractured release is… time beginning at certain controlled conditions compared to the…

TABLE 12 Parameters Affecting the Release Rate of Core …

Coating properties	Density, crystallinity, orier… plasticizer level, cross lin…
Capsule properties	Size, wall thickness, config… coating layers, posttreatm…
Experimental parameters	Temperature, pH, moisture… action, partial pressure d… outside of coating)

Source: Ref. 12.

2 Diffusion

This mechanism acts to limit the release of core material from within the capsule to the surface of the particle by controlling the rate of diffusion of the active compound. The bulk of the capsule material itself may control release (i.e., matrix-controlled release) or a membrane may be added to the capsule for controlling release (i.e., membrane controlled release). Most microcapsules have thin walls, which can function as a semipermeable membrane. Furthermore, because microcapsules are very small, they have a very large surface area per unit weight. Hence, controlled release is frequently accomplished through a diffusion-controlled process [251].

Diffusion release depends upon the kinetic relationship between the core and wall materials and the rate at which the core material is able to pass through the outer wall. It is strictly governed by the chemical properties of the microcapsule and by the physical properties of the wall material such as the matrix structure and pore sizes [249]. Diffusion is a permeation process driven by a concentration gradient or interchain attractive forces [252]. In other words, it is controlled by the solubility of a component in the matrix (this establishes a concentration gradient in the matrix for driving diffusion) and the permeability of the component through the matrix. In the absence of cracks, pinholes, or other flaws, the primary mechanism for core materials to flow through a wall or coating is by activated diffusion, i.e., the penetrant dissolves in the film matrix at the high concentration side, diffuses through the film driven by a concentration gradient (i.e., Fick's law, $J_A = -D_{AB}\, dC_A/dy$, where J_A is the flux of the core material in the y direction, D_{AB} is the diffusivity, and dC_A/dy is the concentration gradient), and evaporates from the other surface. It should be noted that if the food component were not soluble in the matrix, it would not enter the matrix to diffuse through, irrespective of the matrix's pore size.

Diffusion also depends upon the size, shape, vapor pressures, and polarity of the penetrating molecules as well as the segmental motion of polymer chains [252,253]. This also includes interchain attractive forces such as hydrogen bonding and van der Waals interactions, degree of cross-linking, and the amount of crystallinity [254]. In general, cross linking of a matrix has little meaning in most food applications. Very few situations exist where the matrix can be cross-linked considering the limitations imposed by requiring food-approved materials [251]. However, cross-linking of proteins as a consequence of Maillard reactions can occur and possibly influence the diffusion of solutes in heated protein based encapsulation matrices (e.g., gelatin). Thus, the greater the degree of cross-linking, the less the rate of diffusion through the matrix (hence, a readily controllable process of making a controlled release capsule).

The problem of uniform releasing of the aroma of an encapsulated flavor into food should be noted. Because a flavor consists of aroma compounds with a range of volatility, their release, for example, into the head space of a food package, will not be uniform and therefore a balanced characteristic food aroma may not be achieved [255]. The volatility or vapor pressures of these different compounds and their resistances to diffusion will affect their rate. Thus, aromas could become imbalanced as the constituents diffuse through the capsule.

For most physical methods, it is known that the success of encapsulation depends on the formation of a metastable amorphous structure, a glass, with a very low permeability to organic compounds encapsulated within it. In drying processes, the presence of sugar and/or polymers in the encapsulation system reduces the water content. Reduction of water content lowers the glass transition temperature and the resulting amorphous matrix is impermeable to organic compounds as well as to oxygen. However, permeability to water remains finite. This phenomenon, also known as the selective diffusion theory of Thijssen and Rulken [256], is the basis for encapsulation using spray-drying and freeze-drying [247]. In spray-drying, upon droplet formation, rapid evaporation from the surface produces a surface layer in which the selective diffusion mechanism operates. In freeze-drying, upon water crystallization, the nonfrozen solution is viscous and the diffusion of core materials is retarded. At the beginning of freeze-drying, the surface of this solution becomes an amorphous solid in which selective diffusion comes into play.

The permeability of the coating structure can be changed by controlled conditions. The physical state of the food polymer has a considerable role in influencing diffusion and thus release of the core

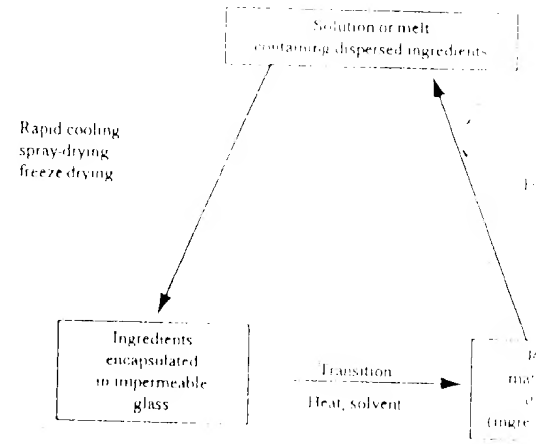


FIGURE 13 Preparation and release of core ingredients from

material. The physicochemical principles governing the softening
lating materials have been studied by several researchers [25
that the release occurs when the glassy, impermeable structure
rubbery state (Fig. 13). Thus, the glass-rubber transition of a ma
ation when evaluating release properties. The relation of transi
of encapsulating formulations has been studied by To and Flink [
in starch-derived encapsulating agents. It must be noted, howeve
ture content or the critical temperature is exceeded, the rate of
content, temperature, and time [262]. This fact allows the genera
The maltodextrins and similar materials with controlled collapse
as encapsulating agents, but are also extremely useful in protecti
logical materials during dehydration and subsequent storage. T
sensitive materials are placed in a medium in which their mobili

3. Solvent-Activated Release

Solvent-activated release is the most common controlled-release
try. Since most encapsulating matrices are water soluble, the water
the microcapsule, thereby liberating its content to the food, or it
begin or enhance the release of the core material. However, wa
dissolved by selecting an appropriate solvent. Encapsulated agen
ucts such as dry beverages and cake and soup mixes. The encaps
released upon rehydration [251]. Their release may be a sudden
livery regulated by controlling the rate of wall solubility, the swell
or changes in the ionic strength of the surrounding medium [249

Although most traditional wall materials will rapidly relea
rehydrated, microcapsule matrices may be modified to release the
in time. Osmotically controlled release is similar to solvent-activ
particle adsorbs a solvent (usually water) over time and swells unt
food ingredient that is first encapsulated in a hydrophilic matrix and
osmotically controlled release functions to a limited extent. The
ally swell and either expand the surface coating, causing cracks

4. Melting-Activated Release

The integrity of the coating can be destroyed by thermal means. This mechanism of release involves the melting of the capsule wall (or a protective coating that has been placed on the capsule wall) to release the active material. Because numerous meltable materials are approved for food use (e.g., lipids, waxes, and modified lipids), this method of release is easily accomplished. Yet the applications are limited. In general, salts, nutrients, leavening agents, and some water-soluble flavoring agents have been protected by hydrophobic coatings to curtail release of the active ingredient into the food until the baking process. The hydrophobic coating and core material must be immiscible with one another in order to avoid migration of the active ingredient through the wall material. This limits the usefulness of the technique for many flavor applications. On the other hand, an already encapsulated flavor prepared by spray-drying can be coated with a hydrophobic matrix via centrifugal coating or the fluidized bed technique. In this manner, the secondary coating on the flavor provides melt release properties [263]. The major problem with this approach, however, is the dilution of the flavoring by additional wall material and the extra cost involved.

5. Biodegradation and pH-Sensitive Release

Release from microcapsules can be accomplished by biodegradation processes if the coatings lend themselves to such degradative mechanisms. Lipid coatings may be degraded by the action of lipases [264]. Karel and Langer [247] released enzymes from liposomes using pH as a stimulant to initiate release. They postulated that pH changes destabilized the phospholipid-based liposomal structure, thereby releasing the enzymes from the liposome core.

VI. CONCLUSIONS

This chapter has focused on the art of microencapsulation and has presented an up-to-date account of the process as it relates to the food industry. Although microencapsulation has been extensively used by the pharmaceutical and chemical industries for many years, its applications to the food industry have lagged and require further improvement. Food ingredients are encapsulated for a variety of reasons including protection from volatilization during storage, protection from undesirable interactions with other food components, minimization of flavor interactions or light-induced deteriorative reactions, and protection against oxidation. Other benefits include ease of handling and mixing, uniform dispersion, and improved product consistency during and after processing. Yet compared with single living cells, the capsules prepared to date are too simplistic, and more development is needed before this technology can be widely applied to the food industry. Because the art of microencapsulation encompasses numerous research fields (e.g., chemistry, engineering, processing, and microbiology), innovative strategies by the food scientist, particularly in the area of controlled release of encapsulated food ingredients, and ever changing technology offer the industry new and exciting areas for research and development.

REFERENCES

1. J. A. Bakan, Microencapsulation, *Encyclopedia of Food Science* (M. S. Peterson and R. Johnson, eds.), AVI Pub. Co., Inc., Westport, CT, 1978, p. 499.
2. C. J. Kirby, Microencapsulation and controlled delivery of food ingredients, *Food Sci. Technol. Today 5*(2):74 (1991).
3. S. M. Barlow, Toxicological aspects of antioxidants used as food additives, *Food Antioxidants* (B. J. F. Hudson, ed.), Elsevier Applied Science, London, 1990, p. 253.
4. A. H. King, Encapsulation of food ingredients: A review of available technology, focusing on hydrocolloids, *Encapsulation and Controlled Release of Food Ingredients* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 590, American Chemical Society, Washington, DC, 1995, p. 26.

5. S. J. Risch, Encapsulation: Overview of uses and techn... *lease of Food Ingredients* (S. J. Risch and G. A. Reinec... 590, American Chemical Society, Washington, DC, 199...
6. C. Andres, Encapsulation ingredients: I, *Food Proc.* 38...
7. R. J. Versic, Flavor encapsulation: An overview, *Flavo...* S. J. Risch, eds.), ACS Symposium Series No. 370, Ameri... 1988, p. 1.
8. T. J. DeZarn, Food ingredient encapsulation: An overview... *of Food Ingredients* (S. J. Risch and G. A. Reineccius, e... American Chemical Society, Washington, DC, 1995, p...
9. R. D. Todd, Microencapsulation and the flavor industry, ...
10. R. E. Sparks, Microencapsulation, *Kirk-Othmer Encyclop...* Vol. 15 (M. Grayson and D. David, eds.), Wiley and So...
11. L. L. Balssa and G. O. Fanger, Microencapsulation in the ... *2*:245 (1971).
12. F. Shahidi and X. Q. Han, Encapsulation of food ingred... (1993).
13. J. A. Bakan, Microencapsulation of foods and related prod...
14. M. A. Godshall, The role of carbohydrates in flavor develop...
15. J. Flink and M. Karel, Effects of process variables on re... *Food Sci. 35*:444 (1970).
16. G. A. Reineccius and S. T. Coulter, Flavor retention durin...
17. G. A. Reineccius, Flavor encapsulation, *Food Rev. Int.* ...
18. G. A. Reineccius, Carbohydrates for flavor encapsulation, ...
19. M. M. Kenyon, Modified starch, maltodextrin, and corn ... encapsulation, *Encapsulation and Controlled Release of F...* Reineccius, eds.), ACS Symposium Series No. 590, Ame... DC, 1995, p. 42.
20. S. Anandaraman and G. A. Reineccius, Stability of encap... *40*(11):88 (1986).
21. W. E. Bangs and G. A. Reineccius, Influence of dryer in... tile flavor compounds during spray drying, *J. Food Sci.* 4...
22. G. A. Reineccius, Part II: Flavor encapsulation, *Sourc...* Reineccius, ed.), Chapman & Hall, New York, 1994, p. ...
23. K. C. M. Raja, B. Sankarikutty, M. Sreekumar, A. Jayal... rial characterization studies of maltodextrin samples for t... (1989).
24. G. A. Reineccius and S. J. Risch, Encapsulation of artifici... *11*(4):1 (1986).
25. J. Solms, Interaction of non-volatile and volatile substance... *ponents* (G. G. Birch and M. G. Lindley, eds.), Elsevier, ...
26. W. King, P. Trubiano, and P. Perry, Modified starch enc... sification, film forming and low surface oil, *Food Prod. ...*
27. P. C. Trubiano and N. L. Lacourse, Emulsion stabilizing ... Risch and G. A. Reineccius, eds.), ACS Symposium Serie... ety, Washington, DC, 1988, p. 45.
28. D. French, The Schardinger dextrins, *Advances in Carb...* Wolfram, ed.), Academic Press, New York, 1957, p. 189.
29. A. R. Hedges, W. J. Shieh, and C. T. Sikorski, Use of c... use and treatment of food products, *Encapsulation and Co...* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium... Society, Washington, DC, 1995, p. 60.

30. D. L. Pszczola, Production and potential food applications of cyclodextrins, *Food Technol. 42*(1):96 (1988).
31. K. Lindner, Using cyclodextrin aroma complexes in catering, *Nahrung 26*:675 (1982).
32. S. Nagamoto, Cyclodextrins. Expanding the development of their functions and applications, *Chem. Econ. Eng. Rev. 17*:28 (1985).
33. J. S. Pagington, β-Cyclodextrin and its uses in the flavor industry, *Developments in Food Flavors* (G. G. Birch and M. G. Lindley, eds.), Elsevier Applied Science Publishers Ltd., London, 1986, p. 131.
34. Vast range of potential uses for cyclodextrins, *Food Eng. 59*:36 (1987).
35. W. Saenger, Cyclodextrin inclusion compounds in research and industry, *Angew. Chemie Int. Ed. 19*:344 (1980).
36. M. W. Nicol, Sucrose in food systems, *Carbohydrate Sweeteners in Food and Nutrition* (P. Koivistoinen and L. Hyvonen, eds.), Academic Press, New York, 1980, p. 151.
37. A. C. Chen, M. F. Veiga, and A. B. Rizzuto, Cocrystallization: An encapsulation process, *Food Technol. 42*(11):87 (1988).
38. G. R. Huber, Carbohydrates in extrusion processing, *Food Technol. 45*(3):160 (1991).
39. Encapsulated spice, seasoning extracts add flavor, color to dry mix products, *Food Eng. 53*(8):67 (1981).
40. Greater stability for encapsulated flavors, *Food Eng. 54*(11):59 (1981).
41. J. W. Marvin, R. A. Berhard, and T. A. Nickerson, Interaction of low molecular weight adsorbents on lactose, *J. Dairy Sci. 62*:1546 (1979).
42. J. A. Kitson and H. S. Sugisawa, Sugar captured flavor granules, *Can. Inst. Food Sci. Technol. J. 7*:15 (1974).
43. A. C. Chen, C. E. Lang, C. P. Graham, and A. B. Rizzuto, Crystalized, readily water-dispersible sugar product, U.S. patent 4,338,350 (1982).
44. A. C. Chen, C. E. Lang, C. P. Graham, and A. B. Rizzuto, Crystallized, readily water-dispersible sugar product containing heat sensitive, acidic or high invert sugar substances, U.S. patent 4,362,757 (1982).
45. D. Knorr and R. A. Teutonico, Chitosan immobilization and permeabilization of *Amaranthus tricolor* cells, *J. Agric. Food Chem. 34*:96 (1986).
46. D. Knorr and J. Berlin, Effects of immobilization and permeabilization procedures on growth of *Chenopodium rubrum* cells and amaranthine concentration, *J. Food Sci. 52*:1397 (1987).
47. Y. Pandya and D. Knorr, Diffusion characteristics and properties of chitosan coacervate capsules, *Proc. Biochem. 26*(2):75 (1991).
48. I. K. Greener and O. Fennema, Barrier properties and surface characteristics of edible, bilayer films, *J. Food Sci. 54*:1393 (1989).
49. I. K. Greener and O. Fennema, Evaluation of edible, bilayer films for use as moisture barriers for food, *J. Food Sci. 54*:1400 (1989).
50. J. J. Kester and O. Fennema, An edible film of lipids and cellulose ethers: Barrier properties to moisture vapor transmission and structural evaluation, *J. Food Sci. 54*:1383 (1989).
51. F. Vojdani and J. A. Torres, Potassium sorbate permeability of polysaccharide films: Chitosan, methylcellulose and hydroxypropyl methylcellulose, *J. Food Proc. Eng. 12*:33 (1990).
52. F. Vojdani and J. A. Torres, Potassium sorbate permeability of methylcellulose and hydroxypropyl methylcellulose coatings. Effect of fatty acids, *J. Food Sci. 55*:841 (1990).
53. D. S. B. Poncelet, D. Poncelet, and R. J. Neufeld, Control of mean diameter and size distribution during formulation of microcapsules with cellulose nitrate membranes, *Enzyme Microb. Technol. 11*:29 (1989).
54. M. Glicksman, Background and classification, *Food Hydrocolloids*, Vol. 1 (M. Glicksman, ed.), CRC Press, Boca Raton, FL, 1982, p. 3.
55. T. J. Carroll, D. Feinerman, R. J. Huzinec, and D. J. Piccolo, Gum composition with plural time releasing flavors and method of preparation, U.S. patent 4,485,118 (1984).
56. M. Glicksman, The hydrocolloids industry in the '80s: Problems and opportunities, *Gums and*

Stabilisers for the Food Industry: Interaction of Hydroc
and P. A. Williams, eds.), Pergmon Press, Oxford, UK
57. M. Glicksman, Food applications of gums, *Food Carbohyd*
eds.), AVI Publishing Co., Inc., Westport, CT, 1982, p
58. J. D. Dziezak, Focus on gums, *Food Technol. 45*(3):11
59. Meiji Seika Kaisha Ltd, Encapsulated liquid foods, Japa
60. I. A. Veliky and M. Kalab, Encapsulation of viscous hig
at ambient temperature, *Food Struct. 9*:151 (1990).
61. Y. Tanaka, Encapsulated food stuffs and process for p
1,489,539 (1977).
62. C. Hoashi, Food product with capsules containing mea
(1989).
63. F. Thevenet, Acacia gums: Stabilizers for flavor encapsula
and G. A. Reineccius, eds.), ACS Symposium Series N
Washington, DC, 1988, p. 37.
64. F. Thevenet, Acacia gums: Natural encapsulation agent f
Controlled Release of Food Ingredients (S. J. Risch and
sium Series No. 590, American Chemical Society, Wash
65. M. Rosenberg and I. J. Kopelman, Microencapsulation of
and potential, Proceedings of the 6th International Cong
1983, p. 142.
66. B. R. Bhandari, E. D. Dumoulin, H. M. J. Richard, I.
capsulation by spray drying: Application to citral and lina
67. T. H. Schultz, J. C. Miers, and W. D. Maclay, Permea
J. Phys. Colloid Chem. 53:1320 (1949).
68. S. L. Kamper and O. Fennema, Water vapor permeabil
49:1478 (1984).
69. S. L. Kamper and O. Fennema, Water vapor permeabili
J. Food Sci. 49:1482 (1984).
70. Food and Drug Administration, United States of America
71. A. P. Tulloch, The composition of beeswax and other w
(1970).
72. A. P. Tulloch and L. L. Hoffman, Canadian beeswax
hydrocarbons, free acids, and long chain esters, *J. Am. C*
73. N. V. Lovergren and R. O. Feuge, Permeability of acetost
Food Chem. 2:558 (1954).
74. H.-D. Belitz and W. Grosch, Lipids, *Food Chemistry*, S
75. K. Koide and M. Karel, Encapsulation and stimulated rele
Int. J. Food Sci. Technol. 22:707 (1987).
76. M. Matsuzaki, F. McCafferty, and M. Karel, The effect
vesicles on the encapsulation and acid resistance of β-galac
Technol. 24:451 (1989).
77. W. F. Hopkins and T. J. Carroll, Encapsulated active ingre
their use in ingested products, European patent applicatio
78. H. H. Hatanaka, Egg lecithin process, U.S. patent 4,844,
79. H. H. Y. Kim and I. C. Baianu, Novel liposome microenc
tions, *Trends Food Sci. Technol. 2*:55 (1991).
80. G. Gregoriadis, Encapsulation of enzymes and other agents
Enzymes (A. J. Andrews, ed.), Royal Society of Chemist
81. F. Szoka and D. Papahadjopoulos, Comparative propertie
vesicles (liposomes), *Annu. Rev. Biophys. Bioeng. 9*:467
82. D. W. Deamer and P. S. Uster, Liposome preparation: Me
J. Ostro, ed.), Marcel Dekker, New York, 1983, p. 27

83. A. D. Bangham, M. W. Hill, and N. G. Miller, Preparation and use of liposomes as models of biological membranes, *Methods Memb. Biol. 1*:1 (1974).
84. M. R. Niesman, Liposome encapsulated manganese chloride as liver specific contrast agent for magnetic resonance imaging, *Diss. Abstr. Int. B 49*:3555 (1989).
85. A. Kondo, Microencapsulation utilizing phase separation from an aqueous solution system, *Microcapsule Processing and Technology* (J. Wade van Valkenburg, ed.), Marcel Dekker, Inc., New York, 1979, p. 70.
86. W. N. Garrett, Y. T. Yang, W. L. Dunkley, and L. M. Smith, Energy utilization, feed-lot performance and fatty acid composition of beef steers fed protein encapsulated tallow or vegetable oils, *J. Animal Sci. 42*:1522 (1976).
87. I. Ono, New encapsulation technique with protein carbohydrate matrix, *J. Jpn. Food Sci. Technol. 27*:529 (1980).
88. I. Ono and Y. Aoyama, Encapsulation and stabilization of oily substances by protein and carbohydrate, *J. Jpn. Food Sci. Technol. 26*:13 (1979).
89. A. H. Taylor, Encapsulation systems and their applications in the flavor industry, *Food Flav. Ingred. Packg. Proc. 5*(9):48 (1983).
90. H. B. Heath, The flavor trap, *Food Flav. Ingred. Packg. Proc. 7*(2):21 (1985).
91. M. Meyers, High performance encapsulation (HPE): Applications in meat processing technology, *Agro Food Industry Hi-Tech* (September/October):23 (1995).
92. D. Blenford, Fully protected, *Food Flav. Ingred. Packg. Proc. 8*(7):43 (1986).
93. W. E. Bangs, Development and characterization of wall materials for spray dried flavorings production, *Diss. Abstr. Int. B 46*(4):1011 (1985).
94. P. J. A. M. Kerkhoff and H. A. C. Thijssen, Retention of aroma components in extractive drying of aqueous carbohydrate solutions, *J. Food Technol. 9*:415 (1974).
95. P. J. A. M. Kerkhoff and H. A. C. Thijssen, The effect of process conditions on aroma retention in drying liquid foods, *Aroma Research*, Proceedings of the International Symposium, Wageningen Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands, 1975, p. 26.
96. L. C. Menting, B. Hoogstad, and H. A. C. Thijssen, Aroma retention during the drying of liquid foods, *J. Food Technol. 5*:127 (1970).
97. J. L. Bomben, B. Bruin, H. A. C. Thijssen, and R. L. Merson, Aroma recovery and retention in concentration and drying of foods, *Adv. Food Res. 20*:1 (1973).
98. G. A. Reineccius and W. E. Bangs, Spray drying of food flavors. III. Optimum infeed concentrations for the retention of artificial flavors, *Perf. Flav. 10*(1):27 (1985).
99. M. M. Leahy, S. Anandaraman, W. E. Bangs, and G. A. Reineccius, Spray drying of food flavors. II. A comparison of encapsulating agents for the drying of artificial flavor, *Perf. Flav. 8*(5):49 (1983).
100. J. Brenner, G. H. Henderson, and R. W. Bergensten, Process of encapsulating an oil and product produced thereby, U.S. patent 3,971,852 (1976).
101. R. Emberger, Aspects of the development of industrial flavor materials, *Flavour '81, Weurman Symposium* (P. de Gruyter Schreier, ed.), Berlin, 1981, p. 620.
102. S. J. Risch and G. A. Reineccius, Spray-dried orange oil: Effect of emulsion size on flavor retention and shelf stability, *Flavor Encapsulation* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 67.
103. Y. I. Chang, J. Scire, and B. Jacobs, Effect of particle size and microstructure properties on encapsulated orange oil, *Flavor Encapsulation* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 87.
104. D. M. Jones, Controlling particle size and release properties: Secondary processing techniques, *Flavor Encapsulation* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 158.
105. J. Brenner, The essence of spray-dried flavors: The state of the art, *Perf. Flav. 8*(2):40 (1983).
106. L. Y. Sheen and S. T. Tsai, Studies on spray-dried microcapsules of ginger, basil and garlic essential oils, *J. Chinese Agric. Chem. Soc. 29*:226 (1991).

107. J. A. Bakan and J. L. Anderson, Microencapsulation, ... *Pharmacy* (L. Lachman, H. A. Lieberman, and J. L. Ka... 1970, p. 384.
108. R. Lamb, Spray chilling, *Food Flav. Ingred. Packg. Pr...*
109. T. H. Schultz, K. P. Dimick, and B. Makower, Incorp... juice powders. I. Locking of citrus oils in sucrose and d...
110. H. E. Swisher, Solid essential oil containing component...
111. H. E. Swisher, Solid essential oil flavoring components, ...
112. F. E. Beck, Essential oils, U.S. patent 3,704,137 (1972...
113. J. M. Barnes and J. A. Steinke, Encapsulation matrix comp... U.S. patent 4,689,235 (1987).
114. D. H. Miller and J. R. Mutka, Preparation of solid esse... 4,499,122 (1985).
115. D. H. Miller and J. R. Mutka, Solid essential oil comp...
116. W. Schlameus, Centrifugal extrusion encapsulation, *Encap... Ingredients* (S. J. Risch and G. A. Reineccius, eds.), A... can Chemical Society, Washington, DC, 1995, p. 96.
117. E. L. Anderson, W. W. Harlowe, L. M. Adams, and M... the production and collection of microcapsules, European...
118. I. J. Kopelman, S. Mevdav, and P. Wilmersdorf, Freeze... citrus aroma, *J. Food Technol. 12*:65 (1977).
119. I. J. Kopelman, D. J. Mangold, and S. Weinberg, Storage... *J. Food Technol. 12*:403 (1977).
120. C. J. Kirby and G. Gregoriadis, A simple procedure fo... encapsulation efficiency under mild conditions, *Liposome Te...* CRC Press, Boca Raton, FL, 1984, p. 19.
121. W. H. Rulkens and H. A. C. Thijssen, Retention volati... malto-dextrin, *J. Food Technol. 7*:79 (1972).
122. J. Flink and M. Karel, Retention of organic volatiles in ... *J. Agric. Food Chem. 18*:295 (1970).
123. J. D. Dziezak, Microencapsulation and encapsulated ingred...
124. L. A. Luzzi and R. J. Gerraughty, Effects of selected var... coacervate capsules, *J. Phar. Sci. 53*:429 (1964).
125. G. R. Chilvers, A. P. Gunning, and V. J. Morris, Coacerva... use in microencapsulation, *Carbohydrate Polym. 8*:55 (19...
126. L. L. Balssa, Flavor encapsulation, U.S. patent 3,495,98...
127. C. Arneodo, A. Baszkin, J. P. Benoit, and C. Thies, Inte... against phases formed by complex coacervation of gelatin, ... G. A. Reineccius, eds.), ACS Symposium Series No. 37... ington, DC, 1988, p. 132.
128. A. H. King, Flavor encapsulation with alginates, *Flavor ...* Reineccius, eds.), ACS Symposium Series No. 370, Ame... DC, 1988, p. 122.
129. R. E. Sparks and N. S. Mason, U.S. patent 4,675,140 (...
130. R. E. Sparks, N. S. Mason, P. Autant, A. Cartillier, and R...
131. R. E. Sparks, I. C. Jacobs, and N. S. Mason, Centrifugal ... ingredients, *Encapsulation and Controlled Release of Foo...* Reineccius, eds.), ACS Symposium Series No. 590, Ame... DC, 1995, p. 87.
132. A. Awad and A. C. Chen, A new generation of sucrose pro... *Technol. 47*(1):146 (1993).
133. J. W. Mullin, Crystallization kinetics, *Crystallization ...* Butterworths, London, 1972, p. 174.

Rizzuto, A. C. Chen, and M. F. Veiga, Modification of the sucrose crystal structure to
enhance pharmaceutical properties of excipient and drug substances, *Pharm. Technol. 8*(9):32 (1984).

135. G. A. Reineccius, Liposomes for controlled release in the food industry, *Encapsulation and Controlled Release of Food Ingredients* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 590, American Chemical Society, Washington, DC, 1995, p. 113.

136. D. Chapman, R. M. Williams, and B. D. Ladbrook, Physical studies of phospholipids: VI. Thermotropic and lyotropic mesomorphism of some 1,2-diacylphosphatidylcholines (lecithin), *Chem. Phys. Lipids 1*:445 (1967).

137. F. Mayhew, S. Conroy, J. King, R. Lazo, G. Nikolopoulus, A. Siciliano, and W. J. Vail, High pressure continuous flow system for drug entrapment in liposomes, *Drug and Enzyme Targeting, Part B* (R. Green and K. J. Widder, eds.), Academic Press, Inc., New York, 1987, p. 64.

138. F. Mayhew, R. Lazo, W. J. Vail, J. King, and A. M. Green, Characterization of liposomes prepared using a microemulsifier, *Biochem. Biophys. Acta 755*:169 (1984).

139. A. Kondo, Microencapsulation by interfacial polymerization, *Microcapsule Processing and Technology* (J. Wade van Valkenburg, ed.), Marcel Dekker, Inc., New York, 1979, p. 35.

140. J. S. Pagington, Molecular encapsulation with β-cyclodextrin, *Food Flav. Ingred. Packg. Proc. 7*(9):51 (1985).

141. P. E. Shaw, J. H. Tatum, and C. W. Wilson, Improved flavor of Navel orange and grapefruit juices by removal of bitter components with β cyclodextrin polymer, *J. Agric. Food Chem. 32*:832 (1984).

142. I. J. Westing, G. A. Reineccius, and F. Caporaso, Shelf life of orange oil: Effects of encapsulation by spray drying, extrusion, and molecular inclusion, *Flavor Encapsulation* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 110.

143. K. Lindner, L. Szente, and J. Szejtli, Food flavoring with β-cyclodextrin complexed flavor substances, *Acta Aliment. 10*:175 (1981).

144. L. Szente and J. Szejtli, Stabilization of flavors by cyclodextrins, *Flavor Encapsulation* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 148.

145. L. Szente, M. Gal Fuzy, and J. Szejtli, Tea aromatization with β cyclodextrin complexed flavors, *Acta Aliment. 17*:193 (1988).

146. J. L. Werner, Encapsulated food acids, *Cereal Foods World 25*(3):102 (1980).

147. W. F. Delaney, Meat color stabilization, U.S. patent 3,560,222 (1971).

148. J. C. Cordray and D. L. Huffman, Restructured pork from hot processed sow meat: Effect of encapsulated food acids, *J. Food Prot. 48*:965 (1985).

149. P. J. Percel and D. W. Perkins, Process of preparing a particulate food acidulant, U.S. patent 4,537,784 (1985).

150. Specially coated natural ingredient improves bread, *Food Proc. 34*(1):10 (1973).

151. J. J. Seighman, Process for encapsulating liquid acids and product, U.S. patent 4,713,251 (1987).

152. W. M. McKernan, Microencapsulation in the flavor industry. I, *Flav. Industry 3*:596 (1972).

153. W. M. McKernan, Microencapsulation in the flavor industry. II, *Flav. Industry 4*:70 (1973).

154. S. Anandaraman and G. A. Reineccius, Microencapsulation of flavor, *Food Flav. Ingred. Packg. Proc. 1*(9):14 (1980).

155. P. Marquardt, Spices, Flavors and aromas, *Eur. Food Drink Rev.* (Autumn):101 (1990).

156. J. S. Jackson and K. Lee, Microencapsulation and the food industry, *Lebens. Wiss. Technol. 24*:289 (1991).

157. J. R. Bedford and D. R. Ashworth, Encapsulated flavors—Their applications and development, *Food Flav. Ingred. Packg. Proc. 5*(2):13 (1983).

158. R. A. Youngs, Spray drying encapsulation—Today's review, *Food Flav. Ingred. Packg. Proc. 8*(10):31 (1986).

159. W. E. Bangs and G. A. Reineccius, Characterization of selected materials for lemon oil encapsulation by spray drying, *J. Food Sci. 55*:1356 (1990).

160. C. I. Beristain, A. Vazquez, H. S. Garcia, and E. J. ... oil by co-crystallization, *Lebens. Wiss. Technol. 29* ...

161. E. L. Magee, Microencapsulation of cheese ripening sy... (1979).

162. E. L. Magee and N. F. Olson, Microencapsulation ... diacetyl and acetol in cheese by encapsulated bacterial c...

163. S. D. Braun, N. F. Olson, and R. C. Lindsay, Micro... to produce acetic acid for enhancement of cheese flav...

164. S. D. Braun and N. F. Olson, Encapsulation of protei... efficiency and temperature and freezing stabilities, *J. A*...

165. C. J. Kirby and B. A. Law, Development in the microe... ogy, *Chemical Aspects of Food Enzymes* (A. T. Andrews ... p. 106.

166. C. J. Kirby, and B. A. Law, Recent development in ... enzyme microencapsulation, *Biotechnology in the Food I*... Online International Ltd., London, UK, 1986, p. 17...

167. Food additives: Microcapsules for flavoring oils, *Fed. R*...

168. Food additives: Microcapsules for flavoring oils, *Fed. Re*...

169. L. L. Balssa and J. Brody, Microencapsulation: The black...

170. E. R. Jensen, Encapsulated flavors, Canadian patent 866,...

171. Microencapsulation extends shelf life of marginally stable m...

172. Lemon flavor for fish survives frying and baking, *Food P*...

173. E. Palmer, Method for encapsulating materials, U.S. pate...

174. W. Abe, Y. Yamamoto, R. Uehara, K. Ogiwara, and I. Sa... safflower oil to milking cows and fattening steers, *Jpn. J.* ...

175. Bush Boake Allen Ltd., Encapsulated flavors, British paten...

176. R. T. Darragh and J. L. Stone, Fats with encapsulated flav...

177. C. Andres, Encapsulated concentrates retain full flavor pro... (1981).

178. How the flavor is sealed, *Food Proc. Ind. 50*(600):36 (198...

179. J. Tuot, Foamed capsules having edible shells enclosing aro... cation GB 2,144,701 A (1985).

180. R. T. Liu, W. R. Nickerson, and C. H. Anderson, Process fo... sules (for various food uses), U.S. patent 4,576,826 (1986).

181. J. Szejtli, L. Szente, and E. Banky Elod, Molecular encapsula... labile flavor substances by cyclodextrins, *Acta Chim. Acad. S*...

182. R. S. Johnson, Encapsulation of volatile liquids, European pa...

183. M. Glass, Sorbitol containing mixture encapsulated flavor, U.S...

184. C. Andres, Unique encapsulation flavors maximize flavor aroma... tard, onion, spices, *Food Proc. 33*(5):23 (1972).

185. Y. C. Wei, S. R. Cherukuri, F. Hriscisce, and D. J. Piccolo, Fla... and sweeteners, long lasting flavored chewing gum compositions... preparation, U.S. patent 4,590,075 (1986).

186. R. K. Yang, Encapsulation composition for use with chewing gum... patent application EP 0,229,000 A2 (1986).

187. J. Szejtli, L. Szente, and E. Szenta, Method for aromatizing tea, ... Swiss patent CH 656,778 A (1986).

188. L. Szente and J. Szejtli, Molecular encapsulation of natural and s... cyclodextrin, *J. Food Sci. 51*:1024 (1986).

189. Heat glaze coating encapsulates flavor, *Food Proc. 30*(6):32 (1969...

190. S. D. Braun, N. F. Olson, and R. C. Lindsay, Production of flavor alcohols from leucine by microencapsulated cell free extracts of ... mutigenes, *J. Food Biochem. 7*:23 (1983).

191. H. Levine, L. Slade, B. V. Lengerich, and J. G. Pickup, Double-encapsulated compositions containing volatile and/or labile components, and processes for preparation and use thereof, U.S. patent 5,087,461 (1992).
192. J. Cea, J. D. Posta, and M. Glass, Encapsulated APM and method of preparation, U.S. patent 4,384,004 (1983).
193. J. Cea, J. D. Posta, and M. Glass, A chewing gum composition incorporating encapsulated L-aspartyl-L-phenylalanine methyl ester, European patent EP 0,067,595 B1 (1987).
194. A. M. Schobel and R. K. Yang, Encapsulated sweeteners composition for use with chewing gum and edible products, U.S. patent 4,824,681 (1989).
195. R. K. Yang and A. M. Schobel, Chewing gum composition with encapsulated sweetener having extended flavor release, U.S. patent 4,911,934 (1990).
196. S. R. Cherukuri and G. Mansukhani, Sweetener delivery systems containing polyvinyl acetate, U.S. patent 4,816,265 (1989).
197. S. R. Cherukuri and G. Mansukhani, Multiple encapsulated sweetener delivery system, U.S. patent 4,933,190 (1990).
198. S. R. Cherukuri, G. Mansukhani, and K. C. Jacob, Stable sweetener delivery system for use with cinnamon flavors, U.S. patent 4,839,184 (1989).
199. A. C. Chen, A. B. Rizzuto, and M. F. Veiga, Cocrystallized sugar nut product, U.S. patent 4,423,085 (1983).
200. A. C. Chen, S. J. Drescher, and C. P. Graham, Maple sugar product and method of preparing and using same, U.S. patent 4,159,210 (1979).
201. J. W. Emmons and R. S. Chapman, Extrusion effects on colors and flavors, *Snack Food 61*(10):40 (1972).
202. I. Ono, Solubilization of fats and oils by solid components of soy sauce. X. Encapsulation and stabilization of oil soluble pigment in a protein-carbohydrate matrix, *J. Jpn. Food Sci. Technol. 26*:346 (1979).
203. P. Cilberto and S. Kramer, Non-caking, water-soluble, granular coated food ingredient, U.S. patent 4,288,460 (1981).
204. F. Shahidi and R. B. Pegg, Encapsulation of the preformed cooked cured meat pigment, *J. Food Sci. 56*:1500 (1981).
205. J. Bitman, L. R. Wrenn, L. P. Dryden, and L. F. Edmondson, Feeding encapsulated vegetable fats to increase the polyunsaturation of milk, cheese, and meat, XIX International Dairy Congress, 1E, 1974, p. 107.
206. L. F. Edmondson, R. A. Yoncoskie, N. H. Rainey, F. W. Douglas, and J. Bitman, Feeding encapsulated oils to increase the polyunsaturation in milk and meat fat, *J. Am. Oil Chem. Soc. 51*(3):72 (1974).
207. V. F. Kristensen, Influence on the fatty acid composition of milk fat on feeding dairy cows increasing amounts of encapsulated soybean oil, XIX International Dairy Congress, 1E, 1974, p. 109.
208. Encapsulated ingredients, *Food Technol. 42*(4):158 (1988).
209. A. P. Simopoulos, Omega 3 fatty acids in health and disease and growth and development. A review, *Am. J. Clin. Nutr. 54*:438 (1991).
210. A. P. Simopoulos, Fatty acids, *Functional Foods, Designer Foods, Pharmafoods, Nutraceuticals* (I. Goldberg, ed.), Chapman & Hall, Glasgow, 1994, p. 355.
211. E. M. Branden and K. K. Carroll, Dietary polyunsaturated fats in relation to mammary carcinogenesis in rats, *Lipids 21*:285 (1986).
212. I. Dyberg, Linolenate derived polyunsaturated fatty acids and prevention of atherosclerosis, *J. Nutr. Rev. 44*:125 (1986).
213. J. Mehta, L. M. Lopez, D. Lowton, and T. Wargovich, Dietary supplementation with omega-3 polyunsaturated fatty acids in patients with stable coronary disease. Effects of indices of platelet and neutrophil function and exercise performance, *Am. J. Med. 84*:45 (1988).
214. V. K. S. Shukla and E. G. Perkins, The presence of oxidative polymeric materials in encapsulated fish oils, *Lipids 26*:23 (1991).

215. F. Gejl-Hansen and J. M. Flink, Freeze-dried carbohydra
Microstructure and fat distribution, *J. Food Sci. 42*:1049
216. K. Taguchi, K. Iwami, F. Ibuki, and M. Kawabata, Oxida
in spray-dried egg white powder and its use in n-3 unsatura
Biosci. Biotech. Biochem. 56:560 (1992).
217. K. Iwami, M. Hattori, S. Nakatani, and F. Ibuki, Spray-dri
acid (microcapsules): Their preservability, digestibility and
Biol. Chem. 51:3301 (1987).
218. F. Shahidi and U. N. Wanasundara, Oxidative stability of
Technology—Physical Chemistry, Modification, and Proce
Tong, eds.), ACS Symposium Series 610, American Chem
p. 139.
219. Hoffmann-La Roche, Inc., Vitamins, Part II: General consi
ence and Technology (Y. H. Hui, ed.), John Wiley and So
220. J. Giese, Vitamin and mineral fortification of foods, *Food*
221. H. S. Hall and R. F. Pondell, Encapsulated nutrients, U.S.
222. Fat matrix encapsulation controls ingredients release reaction
37(5):72 (1976).
223. J. Eden, R. Trksak, and R. Williams, Starch based particula
4,755,397 (1988).
224. L. D. Morse, P. A. Hammes and W. A. Boyd, Devil's food
U.S. Patent 3,821,422 (1974).
225. P. T. Berglund, J. W. Dick, and M. L. Dreher, Effect of
min, riboflavin and niacinamide, and cooking parameters
52:1376 (1987).
226. J. M. deMan, L. deMan, and I. Wygerde, Stability of vi
Milchwissenschaft 41:468 (1986).
227. A. Markus and Z. Pelah, Encapsulation of vitamin A, *J. M*
228. C. Andres, Fat matrix encapsulation controls ingredients re
cific, *Food Proc. 37*(1):72 (1976).
229. S. S. Jackel and F. Belshaw, Encapsulated ferrous sulphate pr
flavors, *Food Proc. 32*(5):28 (1971).
230. B. N. Harrison, G. W. Pla, G. A. Clark, and J. C. Fritz,
enrichment, *Cereal Chem. 53*(1):78 (1976).
231. K. Weingartner, A. Nelson, and J. Erdman, Effect of calci
properties of soy beverages, *J. Food Sci. 48*:256 (1983).
232. M. Hirotsuka, H. Taniguchi, H. Narita, and M. Kito, Calci
cium-lecithin liposome system, *J. Food Sci. 49*:111 (1984).
233. H. W. Schafer, Increasing the recovery of milk proteins in
and encapsulation of enzymes for acceleration of cheese ri
(1975).
234. S. D. Braun, Microencapsulated multi-enzymes to produce
Abstr. Int. B 46:366 (1985).
235. C. J. Kirby, B. E. Brooker, and B. A. Law, Accelerated rip
capsulated enzyme, *Int. J. Food Sci. Technol. 22*:355 (198
236. B. Law and C. Kirby, Microencapsulated enzymes for cheese
J. 53(6):194 (1987).
237. M. El-Soda, L. Pannell, and N. Olson, Microencapsulated e
of cheese ripening, *J. Microencap. 6*:319 (1989).
238. S. C. Kim and N. F. Olson, Production of methanethiol in
taining *Brevibacterium linens* and methionine, *J. Dairy Res*
239. E. P. Cohen, J. J. Halik, R. J. Ravallo, and J. L. Hegadorn
aginous material, U.S. patent 4,275,083 (1981).

240. M. Iso, T. Shirahase, S. Hanamura, S. Urushiyama, and S. Omi, Immobilization of enzyme by microencapsulation and application of the encapsulated enzyme in the catalysis, *J. Microencap. 6*:165 (1989).
241. I. Garcia, R. B. Aisina, O. Ancheta, and C. Pascual, Action of gastric juice on microencapsulated invertase, *Enzyme Microb. Technol. 11*:247 (1989).
242. J. Mansfeld, A. Foerster, A. Schellenberger, and H. Dautzenberg, Immobilization of invertase by encapsulation in polyelectrolyte complexes, *Enzyme Microb. Technol. 13*:240 (1991).
243. Taiyo Chemical Industries Co., Ltd., Encapsulated preservative, Japanese patent 5,136,334 (1976).
244. I. Rozenblat, S. Magdassi, and N. Garti, Effect of electrolytes, stirring and surfactants in the coacervation and microencapsulation (of oleic acid) process in presence of gelatin, *J. Microencap. 6*:515 (1989).
245. D. R. Meyer, Process for preparing a coated particle salt substitute composition, U.S. patent 4,734,290 (1989).
246. D. J. Deeble, B. J. Parsons, and G. O. Phillips, Studies on food antioxidants encapsulated in β-cyclodextrin, *Food and Agriculture: Agricultural Research and Development in Wales*, 6th Conference, Cardiff, UK, 1989, p. 26.
247. M. Karel and R. Langer, Controlled release of food additives, *Flavor Encapsulation* (G. A. Reineccius and S. J. Risch, eds.), ACS Symposium Series No. 370, American Chemical Society, Washington, DC, 1988, p. 177.
248. L. Brannon-Peppas, Controlled release in the food and cosmetic industries, *Polymeric Delivery Systems* (M. A. El-Nokaly, D. M. Piatt, and B. A. Charpentier, eds.), ACS Symposium Series No. 520, American Chemical Society, Washington, DC, 1993, p. 42.
249. C. Whorton, Factors influencing volatile release from encapsulation matrices, *Encapsulation and Controlled Release of Food Ingredients* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 590, American Chemical Society, Washington, DC, 1995, p. 134.
250. D. Pendergrass, The use of controlled delivery in print materials, Second Workshop on the Controlled Delivery in Consumer Products, Controlled Release Society, Secaucus, NJ, May 13-15, 1992.
251. G. A. Reineccius, Controlled release techniques in the food industry, *Encapsulation and Controlled Release of Food Ingredients* (S. J. Risch and G. A. Reineccius, eds.), ACS Symposium Series No. 590, American Chemical Society, Washington, DC, 1995, p. 8.
252. C. Mellenheim and N. Passy, Choice of packages for foods with specific considerations of water activity, *Properties of Water in Foods* (D. Simatos and J. L. Multon, eds.), Martinus Nijhoff Publishing, Dordrecht, The Netherlands, 1985, p. 375.
253. B. Pascat, Study of some factors affecting permeability, *Food Packaging and Preservation: Theory and Practice* (M. Mathlouthi, ed.), Elsevier Applied Science Publishers, London, England, 1986, p. 7.
254. C. A. Kumins, Transport through polymer films, *J. Polym. Sci. Part C 10*:1 (1965).
255. P. I. Lee, Controlled release of volatile multicomponent active agents: Physical considerations, Second Workshop on the Controlled Delivery in Consumer Products, Controlled Release Society, May 13-15, Secaucus, NJ, 1992.
256. H. A. C. Thijssen and W. H. Rulkens, Retention of aromas in drying food liquids, *De Ingenieur 80*(47):45 (1968).
257. M. Karel and J. Flink, Some recent developments in food dehydration research, *Adv. Drying 2*:103 (1983).
258. H. Levine and L. Slade, A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPs), *Carbohydrate Polym. 6*(3):213 (1986).
259. N. Peppas, Diffusional release from polymeric carriers, Second Workshop on the Controlled Delivery in Consumer Products, Controlled Release Society, May 13-15, Secaucus, NJ, 1992.
260. L. Slade and H. Levine, Glass transitions and water food structure interactions, *Advances in Food and Nutrition Research*, Vol. 38 (J. Kinsella, ed.), Academic Press, San Diego, 1994.
261. F. C. To and J. M. Flink, 'Collapse,' a structural transition in freeze dried carbohydrates: I. Evaluation of analytical methods, *J. Food Technol. 13*:551 (1978).

262. M. Karel, Effects of water activity and water content on [illegible] effects on phase transitions in food systems, *Properties* [illegible] Multon, eds.), Martinus Nijhoff Publishing, Dordrecht [illegible]
263. C. T. Tan, Y. C. Kang, M. A. Sudol, C. K. King, an[illegible] trolled release flavors, U.S. patent 5,064,669 (1991).
264. K. Yazawa, R. Arai, M. Kitajima, and A. Kondo, Met[illegible] amino acids, U.S. patent 3,804,776 (1974).